United States
Environmental Protection
Agency

Office of Research and
Development
Washington, DC 20460

EPA/600/R-01/092
September 2001

EPA

Innovative Technology Verification Report

Field Measurement Technologies for Total Petroleum Hydrocarbons in Soil

Dexsil® Corporation PetroFLAG™ System

SITE

EPA/600/R-01/092
September 2001

Innovative Technology Verification Report

Dexsil® Corporation PetroFLAG™ System

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ETV

Notice

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM
VERIFICATION STATEMENT

TECHNOLOGY TYPE:	**FIELD MEASUREMENT DEVICE**
APPLICATION:	**MEASUREMENT OF TOTAL PETROLEUM HYDROCARBONS**
TECHNOLOGY NAME:	**PetroFLAG™ SYSTEM**
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VERIFICATION PROGRAM DESCRIPTION

The U.S. Environmental Protection Agency (EPA) created the Superfund Innovative Technology Evaluation (SITE) and Environmental Technology Verification (ETV) Programs to facilitate deployment of innovative technologies through performance verification and information dissemination. The goal of these programs is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. These programs assist and inform those involved in design, distribution, permitting, and purchase of environmental technologies. This document summarizes results of a demonstration of the PetroFLAG™ System developed by Dexsil ® Corporation (Dexsil).

PROGRAM OPERATION

Under the SITE and ETV Programs, with the full participation of the technology developers, the EPA evaluates and documents the performance of innovative technologies by developing demonstration plans, conducting field tests, collecting and analyzing demonstration data, and preparing reports. The technologies are evaluated under rigorous quality assurance (QA) protocols to produce well-documented data of known quality. The EPA National Exposure Research Laboratory, which demonstrates field sampling, monitoring, and measurement technologies, selected Tetra Tech EM Inc. as the verification organization to assist in field testing seven field measurement devices for total petroleum hydrocarbons (TPH) in soil. This demonstration was funded by the SITE Program.

DEMONSTRATION DESCRIPTION

In June 2000, the EPA conducted a field demonstration of the PetroFLAG™ System and six other field measurement devices for TPH in soil. This verification statement focuses on the PetroFLAG™ System; a similar statement has been prepared for each of the other six devices. The performance and cost of the PetroFLAG™ System were compared to those of an off-site laboratory reference method, "Test Methods for Evaluating Solid Waste" (SW-846) Method 8015B (modified). To verify a wide range of performance attributes, the demonstration had both primary and secondary objectives. The primary objectives included (1) determining the method detection limit, (2) evaluating the accuracy and precision of TPH measurement, (3) evaluating the effect of interferents, and (4) evaluating the effect of moisture content on TPH measurement for each device. Additional primary objectives were to measure sample throughput and estimate TPH measurement costs. Secondary objectives included (1) documenting the skills and training required to properly operate the device, (2) documenting the portability of the device, (3) evaluating the device's durability, and (4) documenting the availability of the device and associated spare parts.

The PetroFLAG™ System was demonstrated by using it to analyze 66 soil environmental samples, 79 soil performance evaluation (PE) samples, and 36 liquid PE samples. In addition to these 181 samples, 10 extract duplicates prepared using the environmental samples were analyzed. The environmental samples were collected in four areas contaminated with gasoline, diesel, or other petroleum products, and the PE samples were obtained from a commercial provider. Dexsil chose not to analyze soil samples collected in a fifth area because Dexsil believed that the natural organic material in the area would adversely impact the PetroFLAG™ System's ability to accurately measure TPH. In addition, Dexsil chose not to analyze

low- and medium-concentration-range weathered gasoline so il PE samples because according to Dexsil, the PetroFLAG™ System was not sensitive to weathered gasoline concentrations of less than 1,000 milligrams per kilogram.

Collectively, the environmental and PE samples provided the di fferent matrix types and the different levels and types of petroleum hydrocarbon contamination needed to perform a comprehensive evaluation of the PetroFLAG™ System. A complete description of the demonstration and a summary of its results are available in the "Innovative Technology Verification Report: Field Measurement Devices fo r Total Petroleum Hydrocarbons in Soil—Dexsil ® Corporation PetroFLAG™ System" (EPA/600/R-01/092).

TECHNOLOGY DESCRIPTION

The PetroFLAG™ System manufactured by Dexsil is based on emulsion turbidimetry, which involves measurement of the light scattered by an emulsion. With the PetroFLAG™ Sy stem, a proprietary, nonpolar, orga nic solvent mixture composed of alcohols, primarily methanol, is used to extract petr oleum hydrocarbons from soil samples. A proprietary developer solution that is polar in nature and that acts as an emulsifier is added to a sample extract in order to precipitate the aromat ic and aliphatic hydrocarbons and form uniformly sized micelles. Light at a wavelength of 585 nanometers is passed through the emulsion, and the amount of light scattered by the emulsion at a 90-degree angle is measured using a turbidimeter. The TPH concentration in the emulsion is then determined by comparing the turbidity reading for the emulsion to that for a reference standard or to a standard calibration curve. Accordi ng to Dexsil, the TPH concentration thus measured is a function of the mean molecular weight of th e hydrocarbons present in the sample.

During the demonstration, extraction of petroleum hydrocarbons in a given soil sample was typically completed by adding 10 milliliters (mL) of proprietary methanol mixture extraction solvent to 10 grams of the sample. To form an emulsion, 2 mL of sample extract was then decanted into a vial containing 4 mL of developer solution. The emulsion was analyzed using the PetroFLAG™ Analyzer (turbidimeter) to obtain a direct measurement of the TPH concentration in the soil sample.

VERIFICATION OF PERFORMANCE

To ensure data usability, data quality indicators for accuracy, precision, representativeness, completeness, and comparability were assessed for the reference method based on project-s pecific QA objectives. Although the reference method results generally exhibited a negative bias, based on the results for the data quality indicators, the reference method results were considered to be of adequate quality. The bias was considered to be significant primarily for low- and medium-concentration-range soil samples containing diesel, which made up only 13 percent of the total number of samples analyzed during the demonstration. The reference method recoveries obs erved during the demonstration were typical of the recoveries obtained by most organic analytical methods for environmental samples. In general, the user should exercise caution when evaluating the accuracy of a field measurement device by comp aring it to reference methods because the reference methods themselves may have limitations. Key demonstration fi ndings are summarized below for the primary objectives.

Method Detection Limit: Based on the TPH results for seven low-concentr ation-range diesel soil PE samples, the method detection limits were determined to be 20 and 6.32 milligrams per kilogram for the PetroFLAG™ System and reference method, respectively.

Accuracy and Precision: Seventy-one of 97 PetroFLAG™ System results (73 percent) used to draw conclusions regarding whether the TPH concentration in a given sampling area or samp le type exceeded a specified action level agreed with those of the reference method; 26 PetroFLAG™ System conclusi ons were false positives. There were no false negatives.

Of 91 PetroFLAG™ System results used to assess measurem ent bias, 11 were within 30 percent, 9 were within 30 to 50 percent, and 71 were not within 50 percent of the refere nce method results; 82 PetroFLAG™ System results were biased high, and 9 were biased low.

For soil environmental samples, the PetroFLAG™ System results were statistically (1) the same as the reference method results for one of the four sampling areas and (2) different fro m the reference method results for three of the sampling areas. For soil PE samples, the PetroFLAG™ System results were sta tistically (1) the same as the reference method results for high-concentration-range diesel samples and (2) different from the reference method results for blank samples, high-concentration-range weathered gasoline samples, and low- and medium-concentr ation-range diesel samples. For liquid PE samples, the PetroFLAG™ System results were statis tically different from the reference method results for both weathered gasoline and diesel samples.

The PetroFLAG™ System results correlated highly with the refe rence method results for one of the four sampling areas and diesel soil PE samples (the square of the correlation coefficient [R^2] values were greater than 0.90, and F-test probability values were less than 5 percent). The PetroFLAG™ System results correlated moderately w ith the reference method results for two of the four sampling areas (R^2 values were 0.84 and 0.86, and F-test pr obability values were less than 5 percent). The PetroFLAG™ System results correlated weakly with the re ference method results for one of the four sampling areas and

weathered gasoline soil PE samples (R^2 values were 0.42 and 0.10, respectively, and F-test probability values were greater than 5 percent).

Comparison of the PetroFLAG™ System and reference method me dian relative standard deviations (RSD) showed that the PetroFLAG™ System and the reference method exhibited sim ilar overall precision. Specifically, the median RSD ranges were 6 to 19 percent and 5.5 to 16 percent for the PetroFLAG™ System and reference method, respectively. The analytical precision was about the same for the PetroFLAG™ System (a me dian relative percent difference of 5) and reference method (a median relative percent difference of 4).

Effect of Interferents: The PetroFLAG™ System showed a mean response of less than 5 percent for neat methyl-tert-butyl ether (MTBE) and tetrachloroethene (PCE) and for soil spiked with humic acid. The device's mean responses for neat Stoddard solvent; turpentine; and 1,2,4-trichlorobenzene were 42. 5, 103, and 16 percent, respectively. The reference method showed varying mean responses for MTBE (39 percent); PC E (17.5 percent); Stoddard solvent (85 percent); turpentine (52 percent); 1,2,4-trichlorobenzene (50 percent); and humic acid (0 percent). For the demonstration, MTBE and Stoddard solvent were included in the definition of TPH.

Effect of Moisture Content: The PetroFLAG™ System showed a statistically significant decrease (17 percent) in TPH results when the soil moisture content was increased from 9 to 16 percent for weathered gasoline soil PE samples; the reference method TPH results were unaffected. Both PetroFLAG™ Sy stem and reference method TPH results were unaffected when the soil moisture content was increased from less than 1 to 9 percent for diesel soil PE samples.

Measurement Time: From the time of sample receipt, Dexsil required 50 hours, 40 minutes, to prepare a draft data package containing TPH results for 181 samples and 10 extract duplicates compared to 30 days for the reference method, which was used to analyze 199 samples and 13 extract duplicates.

Measurement Costs: The TPH measurement cost for 181 samples and 10 extract duplicates was estimated to be $6,390, including the capital equipment purchase cost of $695, for the PetroFLAG™ System compared to $38,560 for the reference method.

Key demonstration findings are summarized below for the secondary objectives.

Skill and Training Requirements: The PetroFLAG™ System can be operated by one person with basic wet chemistry skills. The sample analysis procedure for the device can be learned in the field with a few practice attempts.

Portability: The PetroFLAG™ System is battery-operated and requi res no alternating current power source. The device can be easily moved between sampling areas in the field, if necessary.

Durability and Availability of the Device: All items in the PetroFLAG™ System are available from Dexsil. During a 6-month warranty period, Dexsil will supply replacement parts for the device by overnight courier service at no cost. During the demonstration, none of the device's re usable items malfunctioned or was damaged.

In summary, during the demonstration, the PetroFLAG™ System exhibited the following desirable characteristics of a field TPH measurement device: (1) good precision, (2) lack of sensitiv ity to interferents that are not petroleum hydrocarbons (PCE and humic acid), (3) low measurement costs, and (4) ease of us e. In addition, the PetroFLAG™ System exhibited moderate sample throughput. Based on action level conclusions and st atistical correlations, the PetroFLAG™ System TPH results compared well with those of the reference method; however , the device exhibited a high bias, and its TPH results were determined to be statistically different from those of the refe rence method. In addition, turpentine and 1,2,4-trichlorobenzen e biased the device's TPH results high. Moreover, an increase in soil moisture content biased the device's TPH results low for weathered gasoline soil PE samples. Collectively, the de monstration findings indicated that the user should exercise caution when considering the device for a specific field TPH measurement application.

Original
signed by

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NOTICE: EPA verifications are based on an evaluation of technology performance under specific, predetermined criteria and appropriate quality assurance procedures. The EPA makes no expressed or implied warranties as to the performance of the technology and does not certify that a technology will always operate as verified. The end user is solely responsible for complying with any and all applicable federal, state, and local requirements.

Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's natural resources. Under the mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and scientific support that can be used to solve environmental problems, build the scientific knowledge base needed to manage ecological resources wisely, understand how pollutants affect public health, and prevent or reduce environmental risks.

The National Exposure Research Laboratory (NERL) is the agency's center for investigation of technical and management approaches for identifying and quantifying risks to human health and the environment. Goals of the laboratory's research program are to (1) develop and evaluate methods and technologies for characterizing and monitoring air, soil, and water; (2) support regulatory and policy decisions; and (3) provide the scientific support needed to ensure effective implementation of environmental regulations and strategies.

The EPA's Superfund Innovative Technology Evaluation (SITE) Program evaluates technologies designed for characterization and remediation of contaminated Superfund and Resource Conservation and Recovery Act sites. The SITE Program was created to provide reliable cost and performance data in order to speed acceptance and use of innovative remediation, characterization, and monitoring technologies by the regulatory and user community.

Effective measurement and monitoring technologies are needed to assess the degree of contamination at a site, provide data that can be used to determine the risk to public health or the environment, supply the necessary cost and performance data to select the most appropriate technology, and monitor the success or failure of a remediation process. One component of the EPA SITE Program, the Monitoring and Measurement Technology (MMT) Program, demonstrates and evaluates innovative technologies to meet these needs.

Candidate technologies can originate within the federal government or the private sector. Through the SITE Program, developers are given the opportunity to conduct a rigorous demonstration of their technologies under actual field conditions. By completing the demonstration and distributing the results, the agency establishes a baseline for acceptance and use of these technologies. The MMT Program is administered by the Environmental Sciences Division of NERL in Las Vegas, Nevada.

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Abstract

The PetroFLAG™ System developed by Dexsil® Corporation (Dexsil) was demonstrated under the U.S. Environmental Protection Agency Superfund Innovative Technology Evaluation Program in June 2000 at the Navy Base Ventura County site in Port Hueneme, California. The purpose of the demonstration was to collect reliable performance and cost data for the PetroFLAG™ System and six other field measurement devices for total petroleum hydrocarbons (TPH) in soil. In addition to assessing ease of device operation, the key objectives of the demonstration included determining the (1) method detection limit, (2) accuracy and precision, (3) effects of interferents and soil moisture content on TPH measurement, (4) sample throughput, and (5) TPH measurement costs for each device. The demonstration involved analysis of both performance evaluation (PE) samples and environmental samples collected in four areas contaminated with gasoline, diesel, or other petroleum products. The performance and cost results for a given field measurement device were compared to those for an off-site laboratory reference method, "Test Methods for Evaluating Solid Waste" (SW-846) Method 8015B (modified). During the demonstration, Dexsil required 50 hours, 40 minutes, for TPH measurement of 181 samples and 10 extract duplicates. The TPH measurement costs for these samples were estimated to be $6,390 for the PetroFLAG™ System compared to $38,560 for the reference method. The method detection limits were determined to be 20 and 6.32 milligrams per kilogram for the PetroFLAG™ System and reference method, respectively. During the demonstration, the PetroFLAG™ System exhibited good precision and ease of use. The device's mean responses for interferents that are considered to be petroleum hydrocarbons were mixed (0 and 42.5 percent for neat methyl-tert-butyl ether and Stoddard solvent, respectively). The device's mean responses for interferents that are not considered to be petroleum hydrocarbons were also mixed (1.5, 103, and 16 percent for neat tetrachloroethene; turpentine; and 1,2,4-trichlorobenzene, respectively, and 2.5 percent for soil spiked with humic acid). In addition, an increase in soil moisture content biased the device's TPH results low for weathered gasoline soil PE samples. Based on action level conclusions and statistical correlations, the PetroFLAG™ System TPH results compared well with those of the reference method; however, the device exhibited a high bias, and its TPH results were determined to be statistically different from those of the reference method. Collectively, the demonstration findings indicated that the user should exercise caution when considering the device for a specific field TPH measurement application.

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Abbreviations, Acronyms, and Symbols

>	Greater than
<	Less than
≤	Less than or equal to
±	Plus or minus
μg	Microgram
AC	Alternating current
AEHS	Association for Environmental Health and Sciences
AFB	Air Force Base
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
bgs	Below ground surface
BTEX	Benzene, toluene, ethylbenzene, and xylene
BVC	Base Ventura County
CCV	Continuing calibration verification
CFC	Chlorofluorocarbon
CFR	*Code of Federal Regulations*
DC	Direct current
DER	Data evaluation report
Dexsil	Dexsil® Corporation
DRO	Diesel range organics
EDRO	Extended diesel range organics
EPA	U.S. Environmental Protection Agency
EPH	Extractable petroleum hydrocarbon
ERA	Environmental Resource Associates
FFA	Fuel Farm Area
FID	Flame ionization detector
GC	Gas chromatograph
GRO	Gasoline range organics
ICV	Initial calibration verification
IDW	Investigation-derived waste
ITVR	Innovative technology verification report
kg	Kilogram
L	Liter
LCS	Laboratory control sample
LCSD	Laboratory control sample duplicate
MCAWW	"Methods for Chemical Analysis of Water and Wastes"
MDL	Method detection limit
Means	R.S. Means Company
mg	Milligram
min	Minute

Abbreviations, Acronyms, and Symbols (Continued)

mL	Milliliter
MMT	Monitoring and Measurement Technology
MS	Matrix spike
MSD	Matrix spike duplicate
MTBE	Methyl-tert-butyl ether
n-C_x	Alkane with "x" carbon atoms
NERL	National Exposure Research Laboratory
NEX	Naval Exchange
ng	Nanogram
nm	Nanometer
ORD	Office of Research and Development
ORO	Oil range organics
OSWER	Office of Solid Waste and Emergency Response
PC	Petroleum company
PCB	Polychlorinated biphenyl
PCE	Tetrachloroethene
PE	Performance evaluation
PHC	Petroleum hydrocarbon
PPE	Personal protective equipment
PRA	Phytoremediation Area
PRO	Petroleum range organics
QA	Quality assurance
QC	Quality control
R^2	Square of the correlation coefficient
RPD	Relative percent difference
RSD	Relative standard deviation
SFT	Slop Fill Tank
SITE	Superfund Innovative Technology Evaluation
STL Tampa East	Severn Trent Laboratories in Tampa, Florida
SW-846	"Test Methods for Evaluating Solid Waste"
TPH	Total petroleum hydrocarbons
UST	Underground storage tank
VPH	Volatile petroleum hydrocarbon

Acknowledgments

This report was prepared for the U.S. Environmental Protection Agency (EPA) Superfund Innovative Technology Evaluation Program under the direction and coordination of Dr. Stephen Billets of the EPA National Exposure Research Laboratory (NERL)—Environmental Sciences Division in Las Vegas, Nevada. The EPA NERL thanks Mr. Ernest Lory of Navy Base Ventura County, Ms. Amy Whitley of Kelly Air Force Base, and Mr. Jay Simonds of Handex of Indiana for their support in conducting field activities for the project. Mr. Eric Koglin of the EPA NERL served as the technical reviewer of this report. Mr. Roger Claff of the American Petroleum Institute, Mr. Dominick De Angelis of ExxonMobil Corporation, Dr. Ileana Rhodes of Equilon Enterprises, and Dr. Al Verstuyft of Chevron Research and Technology Company served as the peer reviewers of this report.

This report was prepared for the EPA by Dr. Kirankumar Topudurti and Mr. Eric Monschein of Tetra Tech EM Inc. Special acknowledgment is given to Mr. Jerry Parr of Catalyst Information Resources, L.L.C., for serving as the technical consultant for the project. Additional acknowledgment and thanks are given to Ms. Jeanne Kowalski, Mr. Jon Mann, Mr. Stanley Labunski, and Mr. Joe Abboreno of Tetra Tech EM Inc. for their assistance during the preparation of this report.

Chapter 1
Introduction

The U.S. Environmental Protection Agency (EPA) Office of Research and Development (ORD) National Exposure Research Laboratory (NERL) conducted a demonstration of seven innovative field measurement devices for total petroleum hydrocarbons (TPH) in soil. The demonstration was conducted as part of the EPA Superfund Innovative Technology Evaluation (SITE) Monitoring and Measurement Technology (MMT) Program using TPH-contaminated soil from five areas located in three regions of the United States. The demonstration was conducted at Port Hueneme, California, during the week of June 12, 2000. The purpose of the demonstration was to obtain reliable performance and cost data on field measurement devices in order to provide (1) potential users with a better understanding of the devices' performance and operating costs under well-defined field conditions and (2) the developers with documented results that will assist them in promoting acceptance and use of their devices. The TPH results obtained using the seven field measurement devices were compared to the TPH results obtained from a reference laboratory chosen for the demonstration, which used a reference method modified for the demonstration.

This innovative technology verification report (ITVR) presents demonstration performance results and associated costs for the PetroFLAG™ System developed by Dexsil ® Corporation (Dexsil). Specifically, this report describes the SITE Program, the scope of the demonstration, and the components and definition of TPH (Chapter 1); the innovative field measurement device and the technology upon which it is based (Chapter 2); the three demonstration sites (Chapter 3); the demonstration approach (Chapter 4); the selection of the reference method and laboratory (Chapter 5); the assessment of reference method data quality (Chapter 6); the performance of the field measurement device (Chapter 7); the economic analysis for the field measurement device and reference method (Chapter 8); the demonstration results in summary form (Chapter 9); and the references used to prepare the ITVR (Chapter 10). Supplemental information provided by Dexsil is presented in the appendix.

1.1 Description of SITE Program

Performance verification of innovative environmental technologies is an integral part of the regulatory and research mission of the EPA. The SITE Program was established by the EPA Office of Solid Waste and Emergency Response (OSWER) and ORD under the Superfund Amendments and Reauthorization Act of 1986. The overall goal of the SITE Program is to conduct performance verification studies and to promote the acceptance of innovative technologies that may be used to achieve long-term protection of human health and the environment. The program is designed to meet three primary objectives: (1) identify and remove obstacles to the development and commercial use of innovative technologies, (2) demonstrate promising innovative technologies and gather reliable performance and cost information to support site characterization and cleanup activities, and (3) develop procedures and policies that encourage the use of innovative technologies at Superfund sites as well as at other waste sites or commercial facilities.

The intent of a SITE demonstration is to obtain representative, high-quality performance and cost data on one or more innovative technologies so that potential users can assess the suitability of a given technology for a specific application. The SITE Program includes the following elements:

- **MMT Program**—Evaluates innovative technologies that sample, detect, monitor, or measure hazardous and toxic substances. These technologies are expected

to provide better, faster, or more cost-effective methods for producing real-time data during site characterization and remediation studies than do conventional technologies.

- **Remediation Technology Program**—Conducts demonstrations of innovative treatment technologies to provide reliable performance, cost, and applicability data for site cleanups.

- **Technology Transfer Program**—Provides and disseminates technical information in the form of updates, brochures, and other publications that promote the SITE Program and participating technologies. The Technology Transfer Program also offers technical assistance, training, and workshops to support the technologies. A significant number of these activities are performed by EPA's Technology Innovation Office.

The TPH field measurement device demonstration was conducted as part of the MMT Program, which provides developers of innovative hazardous waste sampling, detection, monitoring, and measurement devices with an opportunity to demonstrate the performance of their devices under actual field conditions. These devices may be used to sample, detect, monitor, or measure hazardous and toxic substances in water, soil gas, soil, and sediment. The technologies include chemical sensors for in situ (in place) measurements, soil and sediment samplers, soil gas samplers, groundwater samplers, field-portable analytical equipment, and other systems that support field sampling or data acquisition and analysis.

The MMT Program promotes acceptance of technologies that can be used to (1) accurately assess the degree of contamination at a site, (2) provide data to evaluate potential effects on human health and the environment, (3) apply data to assist in selecting the most appropriate cleanup action, and (4) monitor the effectiveness of a remediation process. The program places a high priority on innovative technologies that provide more cost-effective, faster, and safer methods for producing real-time or near-real-time data than do conventional, laboratory-based technologies. These innovative technologies are demonstrated under field conditions, and the results are compiled, evaluated, published, and disseminated by the ORD. The primary objectives of the MMT Program are as follows:

- Test and verify the performance of innovative field sampling and analytical technologies that enhance sampling, monitoring, and site characterization capabilities

- Identify performance attributes of innovative technologies to address field sampling, monitoring, and characterization problems in a more cost-effective and efficient manner

- Prepare protocols, guidelines, methods, and other technical publications that enhance acceptance of these technologies for routine use

The MMT Program is administered by the Environmental Sciences Division of the NERL in Las Vegas, Nevada. The NERL is the EPA center for investigation of technical and management approaches for identifying and quantifying risks to human health and the environment. The NERL mission components include (1) developing and evaluating methods and technologies for sampling, monitoring, and characterizing water, air, soil, and sediment; (2) supporting regulatory and policy decisions; and (3) providing the technical support needed to ensure effective implementation of environmental regulations and strategies. By demonstrating innovative field measurement devices for TPH in soil, the MMT Program is supporting the development and evaluation of methods and technologies for field measurement of TPH concentrations in a variety of soil types. Information regarding the selection of field measurement devices for TPH is available in American Petroleum Institute (API) publications (API 1996, 1998).

The MMT Program's technology verification process is designed to conduct demonstrations that will generate high-quality data so that potential users have reliable information regarding device performance and cost. Four steps are inherent in the process: (1) needs identification and technology selection, (2) demonstration planning and implementation, (3) report preparation, and (4) information distribution.

The first step of the verification process begins with identifying technology needs of the EPA and the regulated community. The EPA regional offices, the U.S. Department of Energy, the U.S. Department of Defense, industry, and state environmental regulatory agencies are asked to identify technology needs for sampling, monitoring, and measurement of environmental media. Once a need is identified, a search is conducted to identify

suitable technologies that will address the need. The technology search and identification process consists of examining industry and trade publications, attending related conferences, exploring leads from technology developers and industry experts, and reviewing responses to *Commerce Business Daily* announcements. Selection of technologies for field testing includes evaluation of the candidate technologies based on several criteria. A suitable technology for field testing

- Is designed for use in the field
- Is applicable to a variety of environmentally contaminated sites
- Has potential for solving problems that current methods cannot satisfactorily address
- Has estimated costs that are lower than those of conventional methods
- Is likely to achieve better results than current methods in areas such as data quality and turnaround time
- Uses techniques that are easier or safer than current methods
- Is commercially available

Once candidate technologies are identified, their developers are asked to participate in a developer conference. This conference gives the developers an opportunity to describe their technologies' performance and to learn about the MMT Program.

The second step of the verification process is to plan and implement a demonstration that will generate high-quality data to assist potential users in selecting a technology. Demonstration planning activities include a predemonstration sampling and analysis investigation that assesses existing conditions at the proposed demonstration site or sites. The objectives of the predemonstration investigation are to (1) confirm available information on applicable physical, chemical, and biological characteristics of contaminated media at the sites to justify selection of site areas for the demonstration; (2) provide the technology developers with an opportunity to evaluate the areas, analyze representative samples, and identify logistical requirements; (3) assess the overall logistical requirements for conducting the demonstration; and (4) provide the reference laboratory with an opportunity to identify any matrix-specific analytical problems associated with the contaminated media and to propose appropriate solutions. Information generated through the predemonstration investigation is used to develop the final demonstration design and sampling and analysis procedures.

Demonstration planning activities also include preparing a detailed demonstration plan that describes the procedures to be used to verify the performance and cost of each innovative technology. The demonstration plan incorporates information generated during the predemonstration investigation as well as input from technology developers, demonstration site representatives, and technical peer reviewers. The demonstration plan also incorporates the quality assurance (QA) and quality control (QC) elements needed to produce data of sufficient quality to document the performance and cost of each technology.

During the demonstration, each innovative technology is evaluated independently and, when possible and appropriate, is compared to a reference technology. The performance and cost of one innovative technology are not compared to those of another technology evaluated in the demonstration. Rather, demonstration data are used to evaluate the individual performance, cost, advantages, limitations, and field applicability of each technology.

As part of the third step of the verification process, the EPA publishes a verification statement and a detailed evaluation of each technology in an ITVR. To ensure its quality, the ITVR is published only after comments from the technology developer and external peer reviewers are satisfactorily addressed. In addition, all demonstration data used to evaluate each innovative technology are summarized in a data evaluation report (DER) that constitutes a complete record of the demonstration. The DER is not published as an EPA document, but an unpublished copy may be obtained form the EPA project manager.

The fourth step of the verification process is to distribute information regarding demonstration results. To benefit technology developers and potential technology users, the EPA distributes demonstration bulletins and ITVRs through direct mailings, at conferences, and on the Internet. The ITVRs and additional information on the SITE Program are available on the EPA ORD web site (http://www.epa.gov/ORD/SITE).

1.2 Scope of Demonstration

The purpose of the demonstration was to evaluate field measurement devices for TPH in soil in order to provide (1) potential users with a better understanding of the devices' performance and costs under well-defined field conditions and (2) the developers with documented results that will assist them in promoting acceptance and use of their devices.

Chapter 2 of this ITVR describes both the technology upon which the PetroFLAG™ System is based and the field measurement device itself. Because TPH is a "method-defined parameter," the performance results for the device are compared to the results obtained using an off-site laboratory measurement method—that is, a reference method. Details on the selection of the reference method and laboratory are provided in Chapter 5.

The demonstration had both primary and secondary objectives. Primary objectives were critical to the technology verification and required the use of quantitative results to draw conclusions regarding each field measurement device's performance as well as to estimate the cost of operating the device. Secondary objectives pertained to information that was useful but did not necessarily require the use of quantitative results to draw conclusions regarding the performance of each device. Both the primary and secondary objectives are discussed in Chapter 4.

To meet the demonstration objectives, samples were collected from five individual areas at three sites. The first site is referred to as the Navy Base Ventura County (BVC) site; is located in Port Hueneme, California; and contained three sampling areas. The Navy BVC site lies in EPA Region 9. The second site is referred to as the Kelly Air Force Base (AFB) site; is located in San Antonio, Texas; and contained one sampling area. The Kelly AFB site lies in EPA Region 6. The third site is referred to as the petroleum company (PC) site, is located in north-central Indiana, and contained one sampling area. The PC site lies in EPA Region 5.

In preparation for the demonstration, a predemonstration sampling and analysis investigation was completed at the three sites in January 2000. The purpose of this investigation was to assess whether the sites and sampling areas were appropriate for evaluating the seven field measurement devices based on the demonstration objectives. Demonstration field activities were conducted between June 5 and 18, 2000. The procedures used to verify the performance and costs of the field measurement devices are documented in a demonstration plan completed in June 2000 (EPA 2000). The plan also incorporates the QA/QC elements that were needed to generate data of sufficient quality to document field measurement device and reference laboratory performance and costs. The plan is available through the EPA ORD web site (http://www.epa.gov/ORD/SITE) or from the EPA project manager.

1.3 Components and Definition of TPH

To understand the term "TPH," it is necessary to understand the composition of petroleum and its products. This section briefly describes the composition of petroleum and its products and defines TPH from a measurement standpoint. The organic compounds containing only hydrogen and carbon that are present in petroleum and its derivatives are collectively referred to as petroleum hydrocarbons (PHC). Therefore, in this ITVR, the term "PHC" is used to identify sample constituents, and the term "TPH" is used to identify analyses performed and the associated results (for example, TPH concentrations).

1.3.1 Composition of Petroleum and Its Products

Petroleum is essentially a mixture of gaseous, liquid, and solid hydrocarbons that occur in sedimentary rock deposits. On the molecular level, petroleum is a complex mixture of hydrocarbons; organic compounds of sulfur, nitrogen, and oxygen; and compounds containing metallic constituents, particularly vanadium, nickel, iron, and copper. Based on the limited data available, the elemental composition of petroleum appears to vary over a relatively narrow range: 83 to 87 percent carbon, 10 to 14 percent hydrogen, 0.05 to 6 percent sulfur, 0.1 to 2 percent nitrogen, and 0.05 to 1.5 percent oxygen. Metals are present in petroleum at concentrations of up to 0.1 percent (Speight 1991).

Petroleum in the crude state (crude oil) is a mineral resource, but when refined it provides liquid fuels, solvents, lubricants, and many other marketable products. The hydrocarbon components of crude oil include paraffinic, naphthenic, and aromatic groups. Paraffins (alkanes) are saturated, aliphatic hydrocarbons with straight or branched chains but without any ring structure.

Naphthenes are saturated, aliphatic hydrocarbons containing one or more rings, each of which may have one or more paraffinic side chains (alicyclic hydrocarbons). Aromatic hydrocarbons contain one or more aromatic nuclei, such as benzene, naphthalene, and phenanthrene ring systems, that may be linked with (substituted) naphthenic rings or paraffinic side chains. In crude oil, the relationship among the three primary groups of hydrocarbon components is a result of hydrogen gain or loss between any two groups. Another class of compounds that is present in petroleum products such as automobile gasoline but rarely in crude oil is known as olefins. Olefins (alkenes) are unsaturated, aliphatic hydrocarbons.

The distribution of paraffins, naphthenes, and aromatic hydrocarbons depends on the source of crude oil. For example, Pennsylvania crude oil contains high levels of paraffins (about 50 percent), whereas Borneo crude oil contains less than 1 percent paraffins. As shown in Figure 1-1, the proportion of straight or branched paraffins decreases with increasing molecular weight or boiling point fraction for a given crude oil; however, this is not true for naphthenes or aromatic hydrocarbons. The proportion of monocyclonaphthenes decreases with increasing molecular weight or boiling point fraction, whereas the opposite is true for polycyclonaphthenes (for example, tetralin and decalin) and polynuclear aromatic hydrocarbons; the proportion of mononuclear aromatic hydrocarbons appears to be independent of molecular weight or boiling point fraction.

Various petroleum products consisting of carbon and hydrogen are formed when crude oil is subjected to distillation and other processes in a refinery. Processing of crude oil results in petroleum products with trace quantities of metals and organic compounds that contain nitrogen, sulfur, and oxygen. These products include liquefied petroleum gas, gasoline, naphthas, kerosene, fuel oils, lubricating oils, coke, waxes, and asphalt. Of these products, gasoline, naphthas, kerosene, fuel oils, and lubricating oils are liquids and may be present at petroleum-contaminated sites. Except for gasoline and some naphthas, these products are made primarily by collecting particular boiling point fractions of crude oil from a distillation column. Because this classification of petroleum products is based on boiling point and not on chemical composition, the composition of these products, including the ratio of aliphatic to aromatic hydrocarbons, varies depending on the source of crude oil. In addition, specific information (such as boiling points and carbon ranges) for different petroleum products, varies slightly depending on the source of the information. Commonly encountered forms and blends of petroleum products are briefly described below. The descriptions are primarily based on information in books written by Speight (1991) and Gary and Handwerk (1993). Additional information is provided by Dryoff (1993).

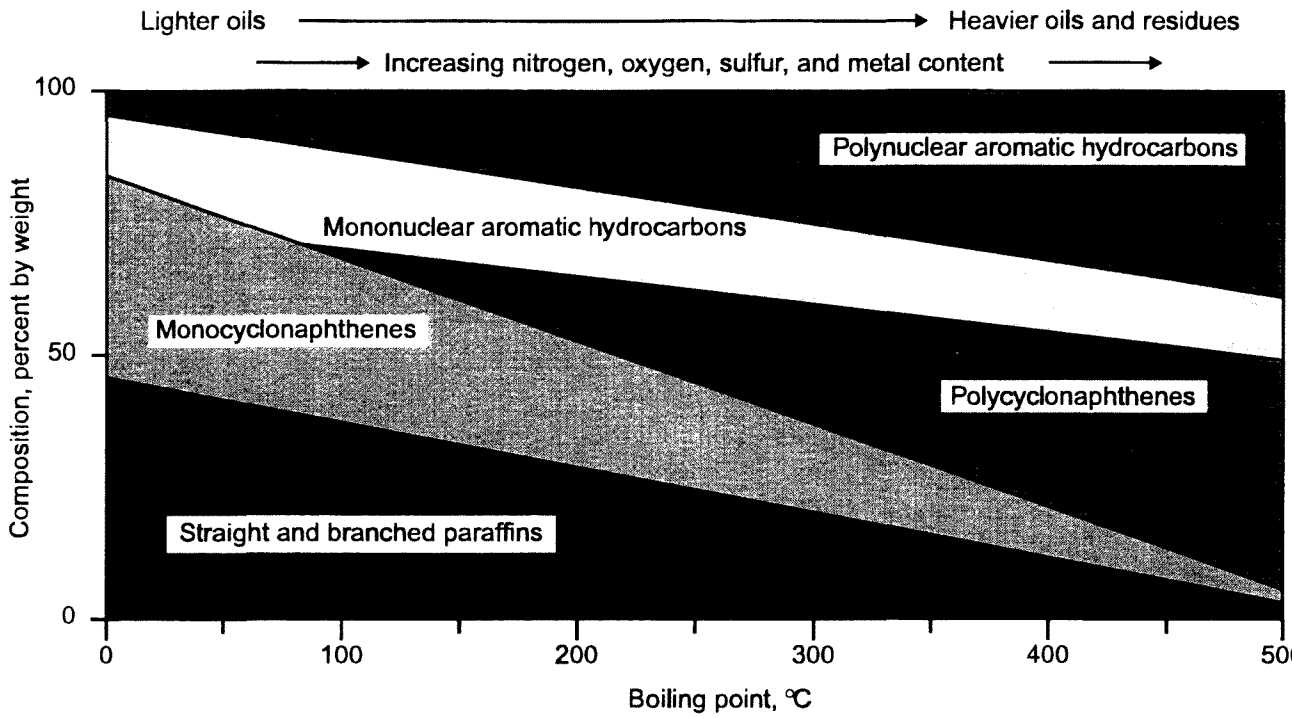
1.3.1.1 Gasoline

Gasoline is a major exception to the boiling point classification described above because "straight-run gasoline" (gasoline directly recovered from a distillation column) is only a small fraction of the blended gasoline that is commercially available as fuel. Commercially available gasolines are complex mixtures of hydrocarbons that boil below 180 °C or at most 225 °C and that contain hydrocarbons with 4 to 12 carbon atoms per molecule. Of the commercially available gasolines, aviation gasoline has a narrower boiling range (38 to 170 °C) than automobile gasoline (-1 to 200 °C). In addition, aviation gasoline may contain high levels of paraffins (50 to 60 percent), moderate levels of naphthenes (20 to 30 percent), a low level of aromatic hydrocarbons (10 percent), and no olefins, whereas automobile gasoline may contain up to 30 percent olefins and up to 40 percent aromatic hydrocarbons.

Gasoline composition can vary widely depending on the source of crude oil. In addition, gasoline composition varies from region to region because of consumer needs for gasoline with a high octane rating to prevent engine "knocking." Moreover, EPA regulations regarding the vapor pressure of gasoline, the chemicals used to produce a high octane rating, and cleaner-burning fuels have affected gasoline composition. For example, when use of tetraethyl lead to produce gasoline with a high octane rating was banned by the EPA, oxygenated fuels came into existence. Production of these fuels included addition of methyl-tert-butyl ether (MTBE), ethanol, and other oxygenates. Use of oxygenated fuels also results in reduction of air pollutant emissions (for example, carbon monoxide and nitrogen oxides).

1.3.1.2 Naphthas

"Naphtha" is a generic term applied to petroleum solvents. Under standardized distillation conditions, at least 10 percent of naphthas should distill below 175 °C, and at least 95 percent of naphthas should distill below 240 °C. Naphthas can be both aliphatic and aromatic and contain



Source: Speight 1991

Figure 1-1. Distribution of various petroleum hydrocarbon types throughout boiling point range of crude oil.

hydrocarbons with 6 to 14 carbon atoms per molecule. Depending on the intended use of a naphtha, it may be free of aromatic hydrocarbons (to make it odor-free) and sulfur (to make it less toxic and less corrosive). Many forms of naphthas are commercially available, including Varnish Makers' and Painters' naphthas (Types I and II), mineral spirits (Types I through IV), and aromatic naphthas (Types I and II). Stoddard solvent is an example of an aliphatic naphtha.

1.3.1.3 Kerosene

Kerosene is a straight-run petroleum fraction that has a boiling point range of 205 to 260 °C. Kerosene typically contains hydrocarbons with 12 or more carbon atoms per molecule. Because of its use as an indoor fuel, kerosene must be free of aromatic and unsaturated hydrocarbons as well as sulfur compounds.

1.3.1.4 Jet Fuels

Jet fuels, which are also known as aircraft turbine fuels, are manufactured by blending gasoline, naphtha, and kerosene in varying proportions. Therefore, jet fuels may contain a carbon range that covers gasoline through kerosene. Jet fuels are used in both military and commercial aircraft. Some examples of jet fuels include Type A, Type A-1, Type B, JP-4, JP-5, and JP-8. The aromatic hydrocarbon content of these fuels ranges from 20 to 25 percent. The military jet fuel JP-4 has a wide boiling point range (65 to 290 °C), whereas commercial jet fuels, including JP-5 and Types A and A-1, have a narrower boiling point range (175 to 290 °C) because of safety considerations. Increasing concerns over combat hazards associated with JP-4 jet fuel led to development of JP-8 jet fuel, which has a flash point of 38 °C and a boiling point range of 165 to 275 °C. JP-8 jet fuel contains hydrocarbons with 9 to 15 carbon atoms per molecule. Type B jet fuel has a boiling point range of 55 to 230 °C and a carbon range of 5 to 13 atoms per molecule. A new specification is currently being developed by the American Society for Testing and Materials (ASTM) for Type B jet fuel.

1.3.1.5 Fuel Oils

Fuel oils are divided into two classes: distillates and residuals. No. 1 and 2 fuel oils are distillates and include kerosene, diesel, and home heating oil. No. 4, 5, and 6 fuel oils are residuals or black oils, and they all contain crude distillation tower bottoms (tar) to which cutter stocks (semirefined or refined distillates) have been added. No. 4 fuel oil contains the most cutter stock, and No. 6 fuel oil contains the least.

Commonly available fuel oils include No. 1, 2, 4, 5, and 6. The boiling points, viscosities, and densities of these fuel oils increase with increasing number designation. The boiling point ranges for No. 1, 2, and 4 fuel oils are about 180 to 320, 175 to 340, and 150 to 480 °C, respectively. No. 1 and 2 fuel oils contain hydrocarbons with 10 to 22 carbon atoms per molecule; the carbon range for No. 4 fuel oil is 22 to 40 atoms per molecule. No. 5 and 6 fuel oils have a boiling point range of 150 to 540 °C but differ in the amounts of residue they contain: No. 5 fuel oil contains a small amount of residue, whereas No. 6 fuel oil contains a large amount. No. 5 and 6 fuel oils contain hydrocarbons with 28 to 90 carbon atoms per molecule. Fuel oils typically contain about 60 percent aliphatic hydrocarbons and 40 percent aromatic hydrocarbons.

1.3.1.6 Diesel

Diesel is primarily used to operate motor vehicle and railroad diesel engines. Automobile diesel is available in two grades: No. 1 and 2. No. 1 diesel, which is sold in regions with cold climates, has a boiling point range of 180 to 320 °C and a cetane number above 50. The cetane number is similar to the octane number of gasoline; a higher number corresponds to less knocking. No. 2 diesel is very similar to No. 2 fuel oil. No. 2 diesel has a boiling point range of 175 to 340 °C and a minimum cetane number of 52. No. 1 diesel is used in high-speed engines such as truck and bus engines, whereas No. 2 diesel is used in other diesel engines. Railroad diesel is similar to No. 2 diesel but has a higher boiling point (up to 370 °C) and lower cetane number (40 to 45). The ratio of aliphatic to aromatic hydrocarbons in diesel is about 5. The carbon range for hydrocarbons present in diesel is 10 to 28 atoms per molecule.

1.3.1.7 Lubricating Oils

Lubricating oils can be distinguished from other crude oil fractions by their high boiling points (greater than 400 °C) and viscosities. Materials suitable for production of lubricating oils are composed principally of hydrocarbons containing 25 to 35 or even 40 carbon atoms per molecule, whereas residual stocks may contain hydrocarbons with 50 to 60 or more (up to 80 or so) carbon atoms per molecule. Because it is difficult to isolate hydrocarbons from the lubricant fraction of petroleum, aliphatic to aromatic hydrocarbon ratios are not well documented for lubricating oils. However, these ratios are expected to be comparable to those of the source crude oil.

1.3.2 Measurement of TPH

As described in Section 1.3.1, the composition of petroleum and its products is complex and variable, which complicates TPH measurement. The measurement of TPH in soil is further complicated by weathering effects. When a petroleum product is released to soil, the product's composition immediately begins to change. The components with lower boiling points are volatilized, the more water-soluble components migrate to groundwater, and biodegradation can affect many other components. Within a short period, the contamination remaining in soil may have only some characteristics in common with the parent product.

This section provides a historical perspective on TPH measurement, reviews current options for TPH measurement in soil, and discusses the definition of TPH that was used for the demonstration.

1.3.2.1 Historical Perspective

Most environmental measurements are focused on identifying and quantifying a particular trace element (such as lead) or organic compound (such as benzene). However, for some "method-defined" parameters, the particular substance being measured may yield different results depending on the measurement method used. Examples of such parameters include oil and grease and surfactants. Perhaps the most problematic of the method-defined parameters is TPH. TPH arose as a parameter for wastewater analyses in the 1960s because of petroleum industry concerns that the original "oil and grease" analytical method, which is gravimetric in nature, might inaccurately characterize petroleum industry wastewaters that contained naturally occurring vegetable oils and greases along with PHCs. These naturally occurring materials are typically long-chain fatty acids (for example, oleic acid, the major component of olive oil).

Originally, TPH was defined as any material extracted with a particular solvent that is not adsorbed by the silica gel used to remove fatty acids and that is not lost when the solvent is evaporated. Although this definition covers most of the components of petroleum products, it includes many other organic compounds as well, including chlorinated solvents, pesticides, and other synthetic organic chemicals. Furthermore, because of the evaporation step in the gravimetric analytical method, the definition excludes most of the petroleum-derived compounds in gasoline that are volatile in nature. For these reasons, an infrared analytical method was developed to measure TPH. In this method, a calibration standard consisting of three components is analyzed at a wavelength of 3.41 micrometers, which corresponds to an aliphatic CH_2 hydrocarbon stretch. As shown in Table 1-1, the calibration standard is designed to mimic a petroleum product having a relative distribution of aliphatic and aromatic compounds as well as a certain percentage of aliphatic CH_2 hydrocarbons. The infrared analytical method indicates that any compound that is extracted by the solvent, is not adsorbed by silica gel, and contains a CH_2 bond is a PHC. Both the gravimetric and infrared analytical methods include an optional, silica gel fractionation step to remove polar, biogenic compounds such as fatty acids, but this cleanup step can also remove some petroleum degradation products that are polar in nature.

In the 1980s, because of the change in focus from wastewater analyses to characterization of hazardous waste sites that contained contaminated soil, many parties began to adapt the existing wastewater analytical methods for application to soil. Unfortunately, the term "TPH" was in common use, as many states had adopted this term (and the wastewater analytical methods) for cleanup activities at underground storage tank (UST) sites. Despite efforts by the API and others to establish new analyte names (for example, gasoline range organics [GRO] and diesel range organics [DRO]), "TPH" is still present in many state regulations as a somewhat ill-defined term, and most state programs still have cleanup criteria for TPH.

1.3.2.2 Current Options for TPH Measurement in Soil

Three widely used technologies measure some form of TPH in soil to some degree. These technologies were used as starting points in deciding how to define TPH for the demonstration. The three technologies and the analytes measured are summarized in Table 1-2.

Of the three technologies, gravimetry and infrared are discussed in Section 1.3.2.1. The third technology, the gas chromatograph/flame ionization detector (GC/FID), came into use because of the documented shortcomings of the other two technologies. The GC/FID had long been used in the petroleum refining industry as a product QC tool to determine the boiling point distribution of pure petroleum products. In the 1980s, environmental laboratories began to apply this technology along with sample preparation methods developed for soil samples to measure PHCs at environmental levels (Zilis, McDevitt, and Parr 1988). GC/FID methods measure all organic compounds that are extracted by the solvent and that can be chromatographed. However, because of method limitations, the very volatile portion of gasoline compounds containing four or five carbon atoms per molecule is not addressed by GC/FID methods; therefore, 100 percent recovery cannot be achieved for pure gasoline. This omission is not considered significant because these low-boiling-point aliphatic compounds (1) are not expected to be present in environmental samples (because of volatilization) and (2) pose less environmental risk than the aromatic hydrocarbons in gasoline.

Table 1-1. Summary of Calibration Information for Infrared Analytical Method

Standard Constituent	Constituent Type	Portion of Constituent in Standard (percent by volume)	Number of Carbon Atoms				Portion of Aliphatic CH_2 in Standard Constituent (percent by weight)
			Aliphatic			Aromatic	
			CH_3	CH_2	CH	CH	
Hexadecane	Straight-chain aliphatic	37.5	2	14	0	0	91
Isooctane	Branched-chain aliphatic	37.5	5	1	1	0	14
Chlorobenzene	Aromatic	25	0	0	0	5	0
Average							35

Table 1-2. Current Technologies for TPH Measurement

Technology	What Is Measured	What Is Not Measured
Gravimetry	All analytes removed from the sample by the extraction solvent that are not volatilized	Volatiles; very polar organics
Infrared	All analytes removed from the sample by the extraction solvent that contain an aliphatic CH_2 stretch	Benzene, naphthalene, and other aromatic hydrocarbons with no aliphatic group attached; very polar organics
Gas chromatograph/flame ionization detector	All analytes removed from the sample by the extraction solvent that can be chromatographed and that respond to the detector	Very polar organics; compounds with high molecular weights or high boiling points

The primary limitation of GC/FID methods relates to the extraction solvent used. The solvent should not interfere with the analysis, but to achieve environmental levels of detection (in the low milligram per kilogram [mg/kg] range) for soil, some concentration of the extract is needed because the sensitivity of the FID is in the nanogram (ng) range. This limitation has resulted in three basic approaches for GC/FID analyses for GRO, DRO, and PHCs.

For GRO analysis, a GC/FID method was developed as part of research sponsored by API and was the subject of an interlaboratory validation study (API 1994); the method was first published in 1990. In this method, GRO is defined as the sum of the organic compounds in the boiling point range of 60 to 170 °C, and the method uses a synthetic calibration standard as both a window-defining mix and a quantitation standard. The GRO method was specifically incorporated into EPA "Test Methods for Evaluating Solid Waste" (SW-846) Method 8015B in 1996 (EPA 1996). The GRO method uses the purge-and-trap technique for sample preparation, effectively limiting the TPH components to the volatile compounds only.

For DRO analysis, a GC/FID method was developed under the sponsorship of API as a companion to the GRO method and was interlaboratory-validated in 1994. In the DRO method, DRO is defined as the sum of the organic compounds in the boiling point range of 170 to 430 °C. As in the GRO method, a synthetic calibration standard is used for quantitation. The DRO method was also incorporated into SW-846 Method 8015B in 1996. The technology used in the DRO method can measure hydrocarbons with boiling points up to 540 °C. However, the hydrocarbons with boiling points in the range of 430 to 540 °C are specifically excluded from SW-846 Method 8015B so as not to include the higher-boiling-point petroleum products. The DRO method uses a solvent extraction and concentration step, effectively limiting the method to nonvolatile hydrocarbons.

For PHC analysis, a GC/FID method was developed by Shell Oil Company (now Equilon Enterprises). This method was interlaboratory-validated along with the GRO and DRO methods in an API study in 1994. The PHC method originally defined PHC as the sum of the compounds in the boiling point range of about 70 to 400 °C, but it now defines PHC as the sum of the compounds in the boiling point range of 70 to 490 °C. The method provides options for instrument calibration, including use of synthetic standards, but it recommends use of products similar to the contaminants present at the site of concern. The PHC method has not been specifically incorporated into SW-846; however, the method has been used as the basis for the TPH methods in several states, including Massachusetts, Washington, and Texas. The PHC method uses solvent microextraction and thus has a higher detection limit than the GRO and DRO methods. The PHC method also begins peak integration after elution of the solvent peak for n-pentane. Thus, this method probably cannot measure some volatile compounds (for example, 2-methyl pentane and MTBE) that are measured using the GRO method.

1.3.2.3 Definition of TPH

It is not possible to establish a definition of TPH that would include crude oil and its refined products and exclude other organic compounds. Ideally, the TPH definition selected for the demonstration would have

- Included compounds that are PHCs, such as paraffins, naphthenes, and aromatic hydrocarbons
- Included, to the extent possible, the major liquid petroleum products (gasoline, naphthas, kerosene, jet fuels, fuel oils, diesel, and lubricating oils)

- Had little inherent bias based on the composition of an individual manufacturer's product
- Had little inherent bias based on the relative concentrations of aliphatic and aromatic hydrocarbons present
- Included much of the volatile portion of gasoline, including all weathered gasoline
- Included MTBE
- Excluded crude oil residuals beyond the extended diesel range organic (EDRO) range
- Excluded nonpetroleum organic compounds (for example, chlorinated solvents, pesticides, polychlorinated biphenyls [PCB], and naturally occurring oils and greases)
- Allowed TPH measurement using a widely accepted method
- Reflected accepted TPH measurement practice in many states

Several states, including Massachusetts, Alaska, Louisiana, and North Carolina, have implemented or are planning to implement a TPH contamination cleanup approach based on the aliphatic and aromatic hydrocarbon fractions of TPH. The action levels for the aromatic hydrocarbon fraction are more stringent than those for the aliphatic hydrocarbon fraction. The approach used in the above-mentioned states involves performing a sample fractionation procedure and two analyses to determine the aliphatic and aromatic hydrocarbon concentrations in a sample. However, in most applications of this approach, only a few samples are subjected to the dual aliphatic and aromatic hydrocarbon analyses because of the costs associated with performing sample fractionation and two analyses.

For the demonstration, TPH was not defined based on the aliphatic and aromatic hydrocarbon fractions because

- Such a definition is used in only a few states.
- Variations exist among the sample fractionation and analysis procedures used in different states.
- The repeatability and versatility of sample fractionation and analysis procedures are not well documented.
- In some states, TPH-based action levels are still used.
- The associated analytical costs are high.

As stated in Section 1.3.2.2, analytical methods currently available for measurement of TPH each exclude some portion of TPH and are unable to measure TPH alone while excluding all other organic compounds, thus making TPH a method-defined parameter. After consideration of all the information presented above, the GRO and DRO analytical methods were selected for TPH measurement for the demonstration. However, because of the general interest in higher-boiling-point petroleum products, the integration range of the DRO method was extended to include compounds with boiling points up to 540 °C. Thus, for the demonstration, the TPH concentration was the sum of all organic compounds that have boiling points between 60 and 540 °C and that can be chromatographed, or the sum of the results obtained using the GRO and DRO methods. This approach accounts for most gasoline, including MTBE, and virtually all other petroleum products and excludes a portion (25 to 50 percent) of the heavy lubricating oils. Thus, TPH measurement for the demonstration included PHCs as well as some organic compounds that are not PHCs. More specifically, TPH measurement did not exclude nonpetroleum organic compounds such as chlorinated solvents, other synthetic organic chemicals such as pesticides and PCBs, and naturally occurring oils and greases. A silica gel fractionation step used to remove polar, biogenic compounds such as fatty acids in some GC/FID methods was not included in the sample preparation step because, according to the State of California, this step can also remove some petroleum degradation products that are also polar in nature (California Environmental Protection Agency 1999). The step-by-step approach used to select the reference method for the demonstration and the project-specific procedures implemented for soil sample preparation and analysis using the reference method are detailed in Chapter 5.

Chapter 2
Description of Emulsion Turbidimetry and the PetroFLAG™ System

Measurement of TPH in soil by field measurement devices generally involves extraction of PHCs from soil using an appropriate solvent followed by measurement of the TPH concentration in the extract using an optical method. An extraction solvent is selected that will not interfere with the optical measurement of TPH in the extract. Some field measurement devices use light in the visible wavelength range, and others use light outside the visible wavelength range (for example, infrared and ultraviolet light).

The optical measurements made by field measurement devices may involve absorbance, reflectance, or fluorescence. In general, the optical measurement for a soil extract is compared to a calibration curve in order to determine the TPH concentration. Calibration curves may be developed by (1) using a series of calibration standards selected based on the type of PHCs being measured at a site or (2) establishing a correlation between off-site laboratory measurements and field measurements for selected, site-specific soil samples.

Field measurement devices may be categorized as quantitative, semiquantitative, and qualitative. These categories are explained below.

- A **quantitative measurement device** measures TPH concentrations ranging from its reporting limit through its linear range. The measurement result is reported as a single, numerical value that has an established precision and accuracy.

- A **semiquantitative measurement device** measures TPH concentrations above its reporting limit. The measurement result may be reported as a concentration range with lower and upper limits.

- A **qualitative measurement device** indicates the presence or absence of PHCs above or below a specified value (for example, the reporting limit or an action level).

The PetroFLAG™ System is a field measurement device capable of providing quantitative TPH measurement results. Measurements made using the PetroFLAG™ System are based on emulsion turbidimetry, which is described in Section 2.1. Two-point calibration curves for the PetroFLAG™ System may be developed using calibration standards. Section 2.2.2 discusses development of calibration curves for the device.

Section 2.1 describes the technology upon which the PetroFLAG™ System is based, Section 2.2 describes the PetroFLAG™ System itself, and Section 2.3 provides Dexsil contact information. The technology and device descriptions presented below are not intended to provide complete operating procedures for measuring TPH concentrations in soil using the PetroFLAG™ System. Detailed operating procedures for the device, including soil extraction, TPH measurement, and TPH concentration calculation procedures, are available from Dexsil. Supplemental information provided by Dexsil is presented in the appendix.

2.1 Description of Emulsion Turbidimetry

Measurement of TPH in soil using the PetroFLAG™ System is based on emulsion turbidimetry. Turbidimetry may be described as measurement of the attenuation, or loss in intensity, of a light beam as the beam passes through a solution with particles large enough to scatter the light. Emulsion turbidimetry involves measurement of the light scattered by an emulsion (in an emulsion, one liquid is stably dispersed in a second, immiscible liquid). The relationship between the amount of light scattered (turbidity) and the concentration of the emulsion may be expressed as shown in Equation 2-1.

$$T = kbc \quad (2\text{-}1)$$

where

T = Turbidity

k = Proportionality constant

b = Light path length (centimeter)

c = Concentration of emulsion (milligram per liter [mg/L])

When PHCs in a soil sample are measured using emulsion turbidimetry, the sample is extracted using a water-miscible solvent, and the sample extract is added to a vial containing an aqueous, polar developer solution. According to Dexsil, the water-miscible solvent extracts all nonpolar hydrocarbons, and the developer solution acts as an emulsifier, causing the aromatic and aliphatic hydrocarbons in solution to precipitate out and form uniformly sized micelles. Micelles are electrically charged, colloidal particles composed of aggregates of large molecules and are stable for some time. The vial containing the resulting emulsion is placed in a turbidimeter to measure the amount of light scattered by the emulsion. In the turbidimeter, light at a wavelength of 585 nanometers (nm) is passed through the emulsion, and the amount of light scattered by the emulsion at a 90-degree angle is measured. A wavelength of 585 nm is typically used because the maximum amount of light is scattered by the emulsion at this wavelength. The total concentration of PHCs in the emulsion is then determined by comparing the turbidity reading for the emulsion to that for a reference standard or to a standard calibration curve prepared using more than one concentration of mineral oil. According to Dexsil, the TPH concentration thus measured is a function of the mean molecular weight of the hydrocarbons present in the sample.

2.2 Description of the PetroFLAG™ System

The PetroFLAG™ System, a quantitative device manufactured by Dexsil, has been commercially available since January 1995. Dexsil currently holds three patents on the device: patent No. 5,756,357; 5,928,950; and 6,117,682. This section describes the device and summarizes its operating procedure.

2.2.1 Device Description

The PetroFLAG™ System extracts PHCs in soil using a proprietary organic solvent mixture composed of alcohols, primarily methanol. The device also uses a proprietary developer solution that is polar in nature and that acts as the emulsifying agent. The developer solution also contains water and surfactants that stabilize the emulsion.

According to Dexsil, the PetroFLAG™ System can be used to measure the petroleum products listed in Table 2-1. Dexsil reports that the device does not distinguish between aromatic and aliphatic hydrocarbons and that it responds to compounds in the C_8 through C_{36} carbon range. Method detection limits (MDL) claimed by Dexsil for the device are also listed in Table 2-1 and range from 10 mg/kg for hydraulic fluid to 1,000 mg/kg for weathered gasoline. In addition, Table 2-1 lists the device's response factors, which are based on mineral oil. The response factors range from 2 for weathered gasoline to 10 for transformer oil, indicating that the device is more sensitive to transformer oil than weathered gasoline. If no information is available regarding the type of contamination in a sample, Dexsil recommends use of an average response factor of 5.

Table 2-1. PetroFLAG™ System Method Detection Limits and Response Factors for Petroleum Products

Petroleum Product	Method Detection Limit (milligram per kilogram)	Response Factor
Mineral oil	15	10
Transformer oil	15	10
Grease	15	9
Hydraulic fluid	10	8
Transmission fluid	19	8
Motor oil	19	7
No. 2 fuel oil	25	7
No. 6 fuel oil	18	6
Diesel	13	5
Gear oil	22	5
Low-aromatic diesel	27	4
Pennsylvania crude oil	20	4
Kerosene	28	4
Jet A fuel	27	4
Weathered gasoline	1,000	2

Source: Dexsil 1997

The PetroFLAG™ System consists of three components: the (1) PetroFLAG™ System starter kit, (2) PetroFLAG™ Reagents kit, and (3) PetroFLAG™ High-Range Extraction Vials kit. The items contained in each

component are listed in Table 2-2. The PetroFLAG™ System starter kit contains both reusable items, including the PetroFLAG™ Analyzer (turbidimeter), digital balance, and digital timer, and enough disposable items, including polypropylene tubes, filter-syringe assemblies, calibration standards, extraction solvent, and developer solution, to perform 10 soil sample analyses. The PetroFLAG™ Reagents kit can be ordered in multiples of the supply requirements for 10 sample analyses. For high-concentration-range samples, the PetroFLAG™ High-Range Extraction Vials kit contains enough proprietary high-range extraction solvent (proprietary glycol ether) and pipettor tips to perform 10 sample extractions. An Eppendorf™ 1-milliliter (mL) pipettor can be purchased separately from Dexsil.

The PetroFLAG™ Analyzer emits light at a factory-preset wavelength of 585 nm. The analyzer is 5.75 inches long, 3.5 inches wide, and 2 inches high and weighs 0.6 pound. The power supply for the analyzer is one 9-volt battery, which according to Dexsil can last for about 18,000 readings.

The PetroFLAG™ Analyzer allows a user in the field to select the response factor that is appropriate for the PHCs suspected to be present at a site. The response factor can be changed at any time without affecting the calibration data stored in the analyzer. The microprocessor in the analyzer uses the calibration data and the response factor selected by the user to convert the optical reading into a TPH concentration in mg/kg. The user is not required to perform any calculations unless a soil to solvent mass ratio other than one is used to measure the TPH concentration or the sample extract is diluted. In such cases, the TPH concentration reported by the analyzer must be multiplied by the dilution factor used.

To assist the user in obtaining accurate TPH measurements, the PetroFLAG™ Analyzer automatically performs several internal checks and informs the user when an error has occurred. For example, if a TPH concentration is outside the linear range of the analyzer but is still within the quantifiable range, the analyzer displays a blinking reading. If the TPH concentration is outside the quantifiable range of the analyzer, the analyzer displays a blinking "EEEE." According to Dexsil, acceptable precision for the linear and quantifiable ranges is plus or minus (±) 10 and ±20 percent precision, respectively.

Table 2-2. PetroFLAG™ System Components

PetroFLAG™ System starter kit
- 1 battery-powered, handheld PetroFLAG™ Analyzer (turbidimeter) (one 9-volt battery included)
- 1 battery-powered ACCULAB® digital balance (one 100-gram calibration weight and two CR2032 cell batteries included)
- 1 battery-powered digital timer (one G-13 button cell battery included)
- 12 plastic screw-capped, polypropylene tubes
- 12 filter-syringe assemblies
- 1 breaktop vial containing zero calibration standard (proprietary methanol mixture)
- 1 breaktop vial containing calibration standard (1,000 milligrams per liter of mineral oil)
- 10 breaktop vials containing extraction solvent (proprietary methanol mixture)
- 10 glass vials containing proprietary developer solution
- User guide
- Training video and interactive compact disk
- Material safety data sheet for proprietary methanol mixture
- Carrying case

PetroFLAG™ Reagents kit
- 12 plastic screw-capped, polypropylene tubes
- 12 filter-syringe assemblies
- 1 breaktop vial containing zero calibration standard (proprietary methanol mixture)
- 1 breaktop vial containing calibration standard (1,000 milligrams per liter of mineral oil)
- 10 breaktop vials containing extraction solvent (proprietary methanol mixture)
- 10 glass vials containing proprietary developer solution
- Material safety data sheet for proprietary methanol mixture

PetroFLAG™ High-Range Extraction Vials kit
- 10 glass vials containing high-range extraction solvent (proprietary glycol ether)
- 10 tips for Eppendorf™ 1-milliliter pipettor

For cases in which a TPH concentration is outside the linear or quantifiable range of the PetroFLAG™ Analyzer, the user must select the most appropriate corrective action from among several options. According to the Dexsil user guide, the user may (1) decrease the soil to solvent mass ratio when the proprietary methanol mixture is used as the solvent or (2) use the high-range extraction solvent (proprietary glycol ether) to generate 1 mL of extract that is subsequently diluted in 10 mL of proprietary methanol mixture. Although it is not mentioned in the user guide, when the TPH concentration is outside the linear range but within the quantifiable range, the user may also dilute the sample extract produced using the proprietary methanol mixture and reanalyze the extract, thus eliminating the re-extraction step and reducing the amount of additional supplies required to perform the TPH measurement.

The PetroFLAG™ Analyzer is also equipped with a built-in temperature sensor that measures the ambient temperature during TPH measurement. The analyzer uses

the sensor's temperature readings to correct for measurement fluctuations caused by temperature variations. However, the temperature corrections are valid only for ambient temperatures within 10 °C of the calibration temperature. Therefore, if the ambient temperature deviates from the calibration temperature by more than 10 °C, an error condition results, and the analyzer has to be recalibrated. According to Dexsil, the operating temperature range for the analyzer is 4 to 45 °C, and the analyzer does not have an operating humidity restriction.

The PetroFLAG™ Analyzer also automatically performs an optical system check. The analyzer has two independent optical channels. During TPH measurement, if the analyzer responses on the two channels are different, the analyzer displays an error message.

Dexsil recommends using its HYDROSCOUT® meter to measure the moisture content of soil samples in the field so that the TPH concentrations can be reported on a dry weight basis. However, for the demonstration, the developers were not required to report TPH concentrations on a dry weight basis; therefore, Dexsil did not use the HYDROSCOUT® meter.

According to Dexsil, 16 analyses can be performed by one field technician using the PetroFLAG™ System in about 1 hour. The device is easy to operate and is designed to be used by those with basic wet chemistry skills. The PetroFLAG™ System starter kit includes a user guide that must be followed to properly operate the device as well as a free training video and interactive compact disk. In addition, during regular business hours, Dexsil provides technical support over the telephone at no additional cost. Depending on the size of a project, Dexsil also provides on-site training upon request.

According to Dexsil, the PetroFLAG™ System is innovative because it responds to a broad range of petroleum products regardless of their composition and extent of weathering. Also, the proprietary methanol solvent mixture used in the device was selected to provide consistent extraction efficiencies for a range of soil types and conditions, including varying levels of moisture content and ionic strength.

2.2.2 Operating Procedure

The PetroFLAG™ System can be calibrated using known standards. During the demonstration, Dexsil generated a two-point calibration curve using an extraction solvent blank (proprietary methanol mixture) for zero calibration and a calibration standard (1,000 mg/L of mineral oil).

During the demonstration, extraction of PHCs in a given soil sample was typically completed by adding 10 mL of proprietary methanol mixture extraction solvent to 10 grams of the sample. If the TPH measurement for a sample was outside the calibration range of the PetroFLAG™ Analyzer, Dexsil either (1) decreased the soil to solvent mass ratio or (2) used the PetroFLAG™ high-range extraction solvent (proprietary glycol ether) to generate 1 mL of extract that was subsequently diluted in 10 mL of proprietary methanol mixture. To form an emulsion, 2 mL of filtered sample extract was then transferred to a vial containing 4 mL of developer solution. The emulsion was analyzed using the PetroFLAG™ Analyzer at a wavelength of 585 nm.

During the demonstration, Dexsil generally used a response factor of 2 for samples containing primarily weathered gasoline and a response factor of 6 for samples containing primarily diesel. When no dilutions were performed, the PetroFLAG™ Analyzer provided a direct measurement of the TPH concentration in a sample; no calculations were required. When a soil to solvent mass ratio other than one was used to measure the TPH concentration in a sample, the concentration reported by the analyzer was multiplied by the dilution factor used.

In addition to the internal checks automatically performed by the PetroFLAG™ Analyzer, Dexsil also analyzed field duplicates and performed a temperature check before analyzing each batch of samples. The temperature check was performed to verify that the PetroFLAG™ Analyzer was operating in an ambient temperature within 5 °C of the calibration temperature. According to Dexsil, although the analyzer automatically performs a temperature check during each measurement to verify that the ambient temperature is within 10 °C of the calibration temperature, TPH measurements made using the analyzer are more accurate when the ambient temperature is within 5 °C of the calibration temperature.

2.3 Developer Contact Information

Additional information about the PetroFLAG™ System can be obtained from the following source:

Dexsil Corporation
Dr. Ted B. Lynn
One Hamden Park Drive
Hamden, CT 06517
Telephone: (203) 288-3509
Fax: (203) 248-6523
E-mail: tblynn@dexsil.com
Internet: www.dexsil.com

Chapter 3
Demonstration Site Descriptions

This chapter describes the three sites selected for conducting the demonstration. The first site is referred to as the Navy BVC site; it is located in Port Hueneme, California, and contains three sampling areas. The second site is referred to as the Kelly AFB site; it is located in San Antonio, Texas, and contains one sampling area. The third site is referred to as the PC site; it is located in north-central Indiana and contains one sampling area. After review of the information available on these and other candidate sites, the Navy BVC, Kelly AFB, and PC sites were selected based on the following criteria:

- **Site Diversity**—Collectively, the three sites contained sampling areas with the different soil types and the different levels and types of PHC contamination needed to evaluate the seven field measurement devices selected for the demonstration.

- **Access and Cooperation**—The site representatives were interested in supporting the demonstration by providing site access for collection of soil samples required for the demonstration. In addition, the field measurement devices were to be demonstrated at the Navy BVC site using soil samples from all three sites, and the Navy BVC site representatives were willing to provide the site support facilities required for the demonstration and to support a visitors' day during the demonstration. As a testing location for the Department of Defense National Environmental Technology Test Site program, the Navy BVC site is used to demonstrate technologies and systems for characterizing or remediating soil, sediment, and groundwater contaminated with fuel hydrocarbons or waste oil.

To ensure that the sampling areas were selected based on current site characteristics, a predemonstration investigation was conducted. During this investigation, samples were collected from the five candidate areas and were analyzed for GRO and EDRO using SW-846 Method 8015B (modified) by the reference laboratory, Severn Trent Laboratories in Tampa, Florida (STL Tampa East). The site descriptions in Sections 3.1 through 3.3 are based on data collected during predemonstration investigation sampling activities, data collected during demonstration sampling activities, and information provided by the site representatives. Physical characterization of samples was performed in the field by a geologist during both predemonstration investigation and demonstration activities.

Some of the predemonstration investigation samples were also analyzed by the PetroFLAG™ System developer, Dexsil, at its facility. Dexsil used reference laboratory and PetroFLAG™ System results to prepare for the demonstration.

Table 3-1 summarizes key site characteristics, including the contamination type, sampling depth intervals, TPH concentration ranges, and soil type in each sampling area. The TPH concentration ranges and soil types presented in Table 3-1 and throughout this report are based on reference laboratory TPH results for demonstration samples and soil characterization completed during the demonstration, respectively. TPH concentration range and soil type information obtained during the demonstration was generally consistent with the information obtained during the predemonstration investigation except for the B-38 Area at Kelly AFB. Additional information on differences between demonstration and predemonstration investigation activities and results is presented in Section 3.2.

Table 3-1. Summary of Site Characteristics

Site	Sampling Area	Contamination Type[a]	Approximate Sampling Depth Interval (foot bgs)	TPH Concentration Range (mg/kg)	Type of Soil
Navy Base Ventura County	Fuel Farm Area	EDRO (weathered diesel with carbon range from n-C_{10} through n-C_{40})	Upper layer[b]	44.1 to 93.7	Medium-grained sand
			Lower layer[b]	8,090 to 15,000	
	Naval Exchange Service Station Area	GRO and EDRO (fairly weathered gasoline with carbon range from n-C_6 through n-C_{14})	7 to 8	28.1 to 280	Medium-grained sand
			8 to 9	144 to 2,570	
			9 to 10	617 to 3,030	
			10 to 11	9.56 to 293	
	Phytoremediation Area	EDRO (heavy lubricating oil with carbon range from n-C_{14} through n-C_{40+})	1.5 to 2.5	1,130 to 2,140	Silty sand
Kelly Air Force Base	B-38 Area	GRO and EDRO (fresh gasoline and diesel or weathered gasoline and trace amounts of lubricating oil with carbon range from n-C_6 through n-C_{40})	23 to 25	43.8 to 193	Sandy clay or silty sand and gravel in upper depth interval and clayey sand and gravel in deeper depth interval
			25 to 27	41.5 to 69.4	
Petroleum company	Slop Fill Tank Area	GRO and EDRO (combination of slightly weathered gasoline, kerosene, JP-5, and diesel with carbon range from n-C_5 through n-C_{32})	2 to 4	6.16 to 3,300	Silty clay with traces of sand and gravel in deeper depth intervals
			4 to 6	37.1 to 3,960	
			6 to 8	43.9 to 1,210	
			8 to 10	52.4 to 554	

Notes:

bgs = Below ground surface
mg/kg = Milligram per kilogram

[a] The beginning or end point of the carbon range identified as "n-C_x" represents an alkane marker consisting of "x" carbon atoms on a gas chromatogram.

[b] Because of soil conditions encountered in the Fuel Farm Area, the sampling depth intervals could not be accurately determined. Sample collection was initiated approximately 10 feet bgs, and attempts were made to collect 4-foot-long soil cores. This approach resulted in varying degrees of core tube penetration up to 17 feet bgs. At each location in the area, the sample cores were divided into two samples based on visual observations. The upper layer of the soil core, which consisted of yellowish-brown, medium-grained sand, made up one sample, and the lower layer of the soil core, which consisted of grayish-black, medium-grained sand and smelled of hydrocarbons, made up the second sample.

3.1 Navy Base Ventura County Site

The Navy BVC site in Port Hueneme, California, covers about 1,600 acres along the south California coast. Three areas at the Navy BVC site were selected as sampling areas for the demonstration: (1) the Fuel Farm Area (FFA), (2) the Naval Exchange (NEX) Service Station Area, and (3) the Phytoremediation Area (PRA). These areas are briefly described below.

3.1.1 Fuel Farm Area

The FFA is a tank farm in the southwest corner of the Navy BVC site. The area contains five tanks and was constructed to refuel ships and to supply heating fuel for the Navy BVC site. Tank No. 5114 along the south edge of the FFA was used to store marine diesel. After Tank No. 5114 was deactivated in 1991, corroded pipelines leading into and out of the tank leaked and contaminated the surrounding soil with diesel.

The horizontal area of contamination in the FFA was estimated to be about 20 feet wide and 90 feet long. Demonstration samples were collected within several inches of the three predemonstration investigation sampling locations in the FFA using a Geoprobe®. Samples were collected at the three locations from east to west and about 5 feet apart. During the demonstration, soil in the area was found to generally consist of medium-grained sand, and the soil cores contained two distinct layers. The upper layer consisted of yellowish-brown, medium-grained sand with no hydrocarbon odor and TPH concentrations ranging from 44.1 to 93.7 mg/kg; the upper layer's TPH concentration range during the predemonstration investigation was 38 to 470 mg/kg. The lower layer consisted of grayish-black, medium-grained sand with a strong hydrocarbon odor and TPH concentrations ranging from 8,090 to 15,000 mg/kg; the lower layer's TPH concentration range during the predemonstration investigation was 7,700 to 11,000 mg/kg.

Gas chromatograms from the predemonstration investigation and the demonstration showed that FFA soil samples contained (1) weathered diesel, (2) hydrocarbons in the n-C_{10} through n-C_{28} carbon range with the hydrocarbon hump maximizing at n-C_{17}, and (3) hydrocarbons in the n-C_{12} through n-C_{40} carbon range with the hydrocarbon hump maximizing at n-C_{20}.

3.1.2 Naval Exchange Service Station Area

The NEX Service Station Area lies in the northeast portion of the Navy BVC site. About 11,000 gallons of regular and unleaded gasoline was released from UST lines in this area between September 1984 and March 1985. Although the primary soil contaminant in this area is gasoline, EDRO is also of concern because (1) another spill north of the area may have resulted in a commingled plume of gasoline and diesel and (2) a significant portion of weathered gasoline is associated with EDRO.

The horizontal area of contamination in the NEX Service Station Area was estimated to be about 450 feet wide and 750 feet long. During the demonstration, samples were collected at the three predemonstration investigation sampling locations in the NEX Service Station Area from south to north and about 60 feet apart using a Geoprobe®. Soil in the area was found to generally consist of (1) brownish-black, medium-grained sand in the uppermost depth interval and (2) grayish-black, medium-grained sand in the three deeper depth intervals. Traces of coarse sand were also present in the deepest depth interval. Soil samples collected from the area had a strong hydrocarbon odor. The water table in the area was encountered at about 9 feet below ground surface (bgs). During the demonstration, TPH concentrations ranged from 28.1 to 280 mg/kg in the 7- to 8-foot bgs depth interval; 144 to 3,030 mg/kg in the 8- to 9- and 9- to 10-foot bgs depth intervals; and 9.56 to 293 mg/kg in the 10- to 11-foot bgs depth interval. During the predemonstration investigation, the TPH concentrations in the (1) top two depth intervals (7 to 8 and 8 to 9 feet bgs) ranged from 25 to 65 mg/kg and (2) bottom depth interval (10 to 11 feet bgs) ranged from 24 to 300 mg/kg.

Gas chromatograms from the predemonstration investigation and the demonstration showed that NEX Service Station Area soil samples contained (1) fairly weathered gasoline with a high aromatic hydrocarbon content and (2) hydrocarbons in the n-C_6 through n-C_{14} carbon range. Benzene, toluene, ethylbenzene, and xylene (BTEX) analytical results for predemonstration investigation samples from the 9- to 10-foot bgs depth interval at the middle sampling location revealed a concentration of 347 mg/kg; BTEX made up 39 percent of the total GRO and 27 percent of the TPH at this location. During the predemonstration investigation, BTEX analyses were conducted at the request of a few developers to estimate the aromatic hydrocarbon content of the GRO; such analyses were not conducted for demonstration samples.

3.1.3 Phytoremediation Area

The PRA lies north of the FFA and west of the NEX Service Station Area at the Navy BVC site. The PRA consists of soil from a fuel tank removal project conducted at the Naval Weapons Station in Seal Beach, California. The area is contained within concrete railings and is 60 feet wide, 100 feet long, and about 3 feet deep. It consists of 12 cells of equal size (20 by 25 feet) that have three different types of cover: (1) unvegetated cover, (2) a grass and legume mix, and (3) a native grass mix. There are four replicate cells of each cover type.

In the PRA, demonstration samples were collected from the 1.5- to 2.5-foot bgs depth interval within several inches of the six predemonstration investigation sampling locations using a split-core sampler. During the demonstration, soil at four adjacent sampling locations was found to generally consist of dark yellowish-brown, silty sand with some clay and no hydrocarbon odor. Soil

at the two remaining adjacent sampling locations primarily consisted of dark yellowish-brown, clayey sand with no hydrocarbon odor, indicating the absence of volatile PHCs. The TPH concentrations in the demonstration samples ranged from 1,130 to 2,140 mg/kg; the TPH concentrations in the predemonstration investigation samples ranged from 1,500 to 2,700 mg/kg.

Gas chromatograms from the predemonstration investigation and the demonstration showed that PRA soil samples contained (1) heavy lubricating oil and (2) hydrocarbons in the n-C_{14} through n-C_{40+} carbon range with the hydrocarbon hump maximizing at n-C_{32}.

Dexsil chose not to demonstrate the PetroFLAG™ System using the soil samples collected in the PRA because Dexsil believed that the natural organic material in the area would adversely impact the device's performance.

3.2 Kelly Air Force Base Site

The Kelly AFB site covers approximately 4,660 acres and is about 7 miles from the center of San Antonio, Texas. One area at Kelly AFB, the B-38 Area, was selected as a sampling area for the demonstration. The B-38 Area lies along the east boundary of Kelly AFB and is part of an active UST farm that serves the government vehicle refueling station at the base. In December 1992, subsurface soil contamination resulting from leaking diesel and gasoline USTs and associated piping was discovered in this area during UST removal and upgrading activities.

The B-38 Area was estimated to be about 150 square feet in size. Based on discussions with site representatives, predemonstration investigation samples were collected in the 13- to 17- and 29- to 30-foot bgs depth intervals at four locations in the area using a Geoprobe®. Based on historical information, the water table in the area fluctuates between 16 and 24 feet bgs. During the predemonstration investigation, soil in the area was found to generally consist of (1) clayey silt in the upper depth interval above the water table with a TPH concentration of 9 mg/kg and (2) sandy clay with significant gravel in the deeper depth interval below the water table with TPH concentrations ranging from 9 to 18 mg/kg. Gas chromatograms from the predemonstration investigation showed that B-38 Area soil samples contained (1) heavy lubricating oil and (2) hydrocarbons in the n-C_{24} through n-C_{30} carbon range.

Based on the low TPH concentrations and the type of contamination detected during the predemonstration investigation as well as discussions with site representatives who indicated that most of the contamination in the B-38 Area can be found at or near the water table, demonstration samples were collected near the water table. During the demonstration, the water table was 24 feet bgs. Therefore, the demonstration samples were collected in the 23- to 25- and 25- to 27-foot bgs depth intervals at three locations in the B-38 Area using a Geoprobe®. Air Force activities in the area during the demonstration prevented the sampling team from accessing the fourth location sampled during the predemonstration investigation.

During the demonstration, soil in the area was found to generally consist of (1) sandy clay or silty sand and gravel in the upper depth interval with a TPH concentration between 43.8 and 193 mg/kg and (2) clayey sand and gravel in the deeper depth interval with TPH concentrations between 41.5 and 69.4 mg/kg. Soil samples collected in the area had little or no hydrocarbon odor. Gas chromatograms from the demonstration showed that B-38 Area soil samples contained either (1) fresh gasoline, diesel, and hydrocarbons in the n-C_6 through n-C_{25} carbon range with the hydrocarbon hump maximizing at n-C_{17}; (2) weathered gasoline with trace amounts of lubricating oil and hydrocarbons in the n-C_6 through n-C_{30} carbon range with a hydrocarbon hump representing the lubricating oil between n-C_{20} and n-C_{30}; or (3) weathered gasoline with trace amounts of lubricating oil and hydrocarbons in the n-C_6 through n-C_{40} carbon range with a hydrocarbon hump representing the lubricating oil maximizing at n-C_{31}.

3.3 Petroleum Company Site

One area at the PC site in north-central Indiana, the Slop Fill Tank (SFT) Area, was selected as a sampling area for the demonstration. The SFT Area lies in the west-central portion of the PC site and is part of an active fuel tank farm. Although the primary soil contaminant in this area is gasoline, EDRO is also of concern because of a heating oil release that occurred north of the area.

The SFT Area was estimated to be 20 feet long and 20 feet wide. In this area, demonstration samples were collected from 2 to 10 feet bgs at 2-foot depth intervals within several inches of the five predemonstration investigation

sampling locations using a Geoprobe®. Four of the sampling locations were spaced 15 feet apart to form the corners of a square, and the fifth sampling location was at the center of the square. During the demonstration, soil in the area was found to generally consist of brown to brownish-gray, silty clay with traces of sand and gravel in the deeper depth intervals. Demonstration soil samples collected in the area had little or no hydrocarbon odor. During the demonstration, soil in the three upper depth intervals had TPH concentrations ranging from 6.16 to 3,960 mg/kg, and soil in the deepest depth interval had TPH concentrations ranging from 52.4 to 554 mg/kg. During the predemonstration investigation, soils in the three upper depth intervals and the deepest depth interval had TPH concentrations ranging from 27 to 1,300 mg/kg and from 49 to 260 mg/kg, respectively.

Gas chromatograms from the predemonstration investigation and the demonstration showed that SFT Area soil samples contained (1) slightly weathered gasoline, kerosene, JP-5, and diesel and (2) hydrocarbons in the n-C_5 through n-C_{20} carbon range. There was also evidence of an unidentified petroleum product containing hydrocarbons in the n-C_{24} through n-C_{32} carbon range. BTEX analytical results for predemonstration investigation samples from the deepest depth interval revealed concentrations of 26, 197, and 67 mg/kg at the northwest, center, and southwest sampling locations, respectively. At the northwest location, BTEX made up 13 percent of the total GRO and 5 percent of the TPH. At the center location, BTEX made up 16 percent of the total GRO and 7 percent of the TPH. At the southwest location, BTEX made up 23 percent of the total GRO and 18 percent of the TPH. BTEX analyses were not conducted for demonstration samples.

Chapter 4
Demonstration Approach

This chapter presents the objectives (Section 4.1), design (Section 4.2), and sample preparation and management procedures (Section 4.3) for the demonstration.

4.1 Demonstration Objectives

The primary goal of the SITE MMT Program is to develop reliable performance and cost data on innovative, field-ready technologies. A SITE demonstration must provide detailed and reliable performance and cost data so that potential technology users have adequate information to make sound judgments regarding an innovative technology's applicability to a specific site and to compare the technology to conventional technologies.

The demonstration had both primary and secondary objectives. Primary objectives were critical to the technology evaluation and required the use of quantitative results to draw conclusions regarding a technology's performance. Secondary objectives pertained to information that was useful but did not necessarily require the use of quantitative results to draw conclusions regarding a technology's performance.

The primary objectives for the demonstration of the individual field measurement devices were as follows:

P1. Determine the MDL

P2. Evaluate the accuracy and precision of TPH measurement for a variety of contaminated soil samples

P3. Evaluate the effect of interferents on TPH measurement

P4. Evaluate the effect of soil moisture content on TPH measurement

P5. Measure the time required for TPH measurement

P6. Estimate costs associated with TPH measurement

The secondary objectives for the demonstration of the individual field measurement devices were as follows:

S1. Document the skills and training required to properly operate the device

S2. Document health and safety concerns associated with operating the device

S3. Document the portability of the device

S4. Evaluate the durability of the device based on its materials of construction and engineering design

S5. Document the availability of the device and associated spare parts

The objectives for the demonstration were developed based on input from MMT Program stakeholders, general user expectations of field measurement devices, characteristics of the demonstration areas, the time available to complete the demonstration, and device capabilities that the developers intended to highlight.

4.2 Demonstration Design

A predemonstration sampling and analysis investigation was conducted to assess existing conditions and confirm available information on physical and chemical characteristics of soil in each demonstration area. Based on information from the predemonstration investigation as well as available historical data, a demonstration design was developed to address the demonstration objectives. Input regarding the demonstration design was obtained

from the developers and demonstration site representatives. The demonstration design is summarized below.

The demonstration involved analysis of soil environmental samples, soil performance evaluation (PE) samples, and liquid PE samples. The environmental samples were collected from three contaminated sites, and the PE samples were obtained from a commercial provider, Environmental Resource Associates (ERA) in Arvada, Colorado. Collectively, the environmental and PE samples provided the different matrix types and the different levels and types of PHC contamination needed to perform a comprehensive demonstration.

The environmental samples were soil core samples collected from the demonstration areas at the Navy BVC, Kelly AFB, and PC sites described in Chapter 3. The soil core samples collected at the Kelly AFB and PC sites were shipped to the Navy BVC site 5 days prior to the start of the field analysis activities. Each soil core sample collected from a specific depth interval at a particular sampling location in a given area was homogenized and placed in individual sample containers. Soil samples were then provided to the developers and reference laboratory. In addition, the PE samples were obtained from ERA for distribution to the developers and reference laboratory. Field analysis of all environmental and PE samples was conducted near the PRA at the Navy BVC site.

The field measurement devices were evaluated based primarily on how they compared with the reference method selected for the demonstration. PE samples were used to verify that reference method performance was acceptable. However, for the comparison with the device results, the reference method results were not adjusted based on the recoveries observed during analysis of the PE samples.

The sample collection and homogenization procedures may have resulted in GRO losses of up to one order of magnitude in environmental samples. Despite any such losses, the homogenized samples were expected to contain sufficient levels of GRO to allow demonstration objectives to be achieved. Moreover, the environmental sample collection and homogenization procedures implemented during the demonstration ensured that the developers and reference laboratory received the same sample material for analysis, which was required to allow meaningful comparisons of field measurement device and reference method results.

To facilitate effective use of available information on both the environmental and PE samples during the demonstration, the developers and reference laboratory were informed of (1) whether each sample was an environmental or PE sample, (2) the area where each environmental sample was collected, and (3) the contamination type and concentration range of each sample. This information was included in each sample identification number. Each sample was identified as having a low (less than 100 mg/kg), medium (100 to 1,000 mg/kg), or high (greater than 1,000 mg/kg) TPH concentration range. The concentration ranges were based primarily on predemonstration investigation results or the amount of weathered gasoline or diesel added during PE sample preparation. The concentration ranges were meant to be used only as a guide by the developers and reference laboratory. The gasoline used for PE sample preparation was 50 percent weathered; the weathering was achieved by bubbling nitrogen gas into a known volume of gasoline until the volume was reduced by 50 percent. Some PE samples also contained interferents specifically added to evaluate the effect of interferents on TPH measurement. The type of contamination and expected TPH concentration ranges were identified; however, the specific compounds used as interferents were not identified. All PE samples were prepared in triplicate as separate, blind samples.

During the demonstration, Dexsil field technician's operated the PetroFLAG™ System, and EPA representatives made observations to evaluate the device. All the developers were given the opportunity to choose not to analyze samples collected in a particular area or a particular class of samples, depending on the intended uses of their devices. Dexsil chose not to analyze soil samples collected in the PRA because Dexsil believed that the natural organic material in the area would adversely impact the PetroFLAG™ System's ability to accurately measure TPH. In addition, Dexsil chose not to analyze low- and medium-concentration-range weathered gasoline soil PE samples because according to Dexsil, the PetroFLAG™ System was not sensitive to weathered gasoline concentrations of less than 1,000 mg/kg.

Details of the approach used to address the primary and secondary objectives for the demonstration are presented in Sections 4.2.1 and 4.2.2, respectively.

4.2.1 *Approach for Addressing Primary Objectives*

This section presents the approach used to address each primary objective.

Primary Objective P1: Method Detection Limit

To determine the MDL for each field measurement device, low-concentration-range soil PE samples containing weathered gasoline or diesel were to be analyzed. The low-range PE samples were prepared using methanol, which facilitated preparation of homogenous samples. The target concentrations of the PE samples were set to meet the following criteria: (1) at the minimum acceptable recoveries set by ERA, the samples contained measurable TPH concentrations, and (2) when feasible, the sample TPH concentrations were generally between 1 and 10 times the MDLs claimed by the developers and the reference laboratory, as recommended by 40 *Code of Federal Regulations* (CFR) Part 136, Appendix B, Revision 1.1.1. Dexsil and the reference laboratory analyzed seven diesel PE samples to statistically determine the MDLs for EDRO soil samples. Dexsil chose not to analyze the low-range weathered gasoline PE samples because according to Dexsil, the PetroFLAG™ System was not sensitive to weathered gasoline concentrations of less than 1,000 mg/kg. The reference laboratory analyzed seven low-range weathered gasoline PE samples; however, during the preparation of these samples, significant volatilization of PHCs occurred because of the matrix used for preparing the samples. Because of the problems associated with preparation of low-range weathered gasoline PE samples, the results for these samples could not be used to determine the MDL for the reference method.

Primary Objective P2: Accuracy and Precision

To estimate the accuracy and precision of each field measurement device, both environmental and PE samples were analyzed. The evaluation of analytical accuracy was based on the assumption that a field measurement device may be used to (1) determine whether the TPH concentration in a given area exceeds an action level or (2) perform a preliminary characterization of soil in a given area. To evaluate whether the TPH concentration in a soil sample exceeded an action level, the developers and reference laboratory were asked to determine whether TPH concentrations in a given area or PE sample type exceeded the action levels listed in Table 4-1. The action levels chosen for environmental samples were based on the predemonstration investigation analytical results and state action levels. The action levels chosen for the PE samples were based in part on the ERA acceptance limits

Table 4-1. Action Levels Used to Evaluate Analytical Accuracy

Site	Area	Typical TPH Concentration Range[a]	Action Level (mg/kg)
Navy Base Ventura County	Fuel Farm Area	Low and high	100
	Naval Exchange Service Station Area	Low to high	50
	Phytoremediation Area[b]	High	1,500
Kelly Air Force Base	B-38 Area	Low	100
Petroleum company	Slop Fill Tank Area	Medium	500
Performance evaluation samples (GRO analysis)		Medium	200
		High	2,000
Performance evaluation samples (EDRO analysis)		Low	15
		Medium	200
		High	2,000

Notes:

mg/kg = Milligram per kilogram

[a] The typical TPH concentration ranges shown cover all the depth intervals in each area. Table 4-2 shows the depth intervals that were sampled in each area and the typical TPH concentration range for each depth interval. The action level for each area was used as the basis for evaluating sample analytical results regardless of the typical TPH concentration ranges for the various depth intervals.

[b] Dexsil chose not to analyze soil samples collected in the Phytoremediation Area because Dexsil believed that the natural organic material in the area would adversely impact the PetroFLAG™ System's ability to accurately measure TPH.

for PE samples; therefore, each PE sample was expected to have at least the TPH concentration indicated in Table 4-1. As stated above, Dexsil did not analyze low- and medium-concentration-range weathered gasoline soil PE samples, so primary objective P2 could not be addressed for the PetroFLAG™ System based on these samples. In addition, because of the problems associated with preparation of the low-range weathered gasoline PE samples, the results for these samples could not be used to address primary objective P2 for the reference method.

Neat (liquid) samples of weathered gasoline and diesel were also analyzed by the developers and reference laboratory to evaluate accuracy and precision. Because extraction of the neat samples was not necessary, the results for these samples provided accuracy and precision information strictly associated with the analyses and were not affected by extraction procedures.

Sample TPH results obtained using each field measurement device and the reference method were compared to the action levels presented in Table 4-1 in order to determine whether sample TPH concentrations were above the action levels. The results obtained using the device and reference method were compared to determine how many times the device's results agreed with those of the reference method for a particular area or sample type. In addition, the ratio of the TPH results of a given device to the TPH results of the reference method was calculated. The ratio was used to develop a frequency distribution in order to determine how many of the device and reference method results were within 30 percent, within 50 percent, and outside the 50 percent window.

To complete a preliminary characterization of soil in a given area using a field measurement device, the user may have to demonstrate to a regulatory agency that (1) no statistically significant difference exists between the results of the laboratory method selected for the project (the reference method) and the device results, indicating that the device may be used as a substitute for the laboratory method, or (2) a consistent correlation exists between the device and laboratory method results, indicating that the device results can be adjusted using the established correlation.

To evaluate whether a statistically significant difference existed between a given field measurement device and the reference method results, a two-tailed, paired Student's t-test was performed. To determine whether a consistent correlation existed between the TPH results of a given field measurement device and the reference method, a linear regression was performed to estimate the square of the correlation coefficient (R^2), the slope, and the intercept of each regression equation. Separate regression equations were developed for each demonstration area and for the PE samples that did not contain interferents. The reliability of the regression equations was tested using the F-test; the regression equation probability derived from the F-test was used to evaluate whether the correlation between the TPH results of the device and the reference method occurred merely by chance.

To evaluate analytical precision, one set of blind field triplicate environmental samples was collected from each depth interval at one location in each demonstration area except the B-38 Area, where site conditions allowed collection of triplicates in the top depth interval only. Blind triplicate low-, medium-, and high-concentration-range PE samples were also used to evaluate analytical precision because TPH concentrations in environmental samples collected during the demonstration sometimes differed from the analytical results for predemonstration investigation samples. The low- and medium-range PE samples were prepared using methanol as a carrier, which facilitated preparation of homogenous samples.

Additional information regarding analytical precision was collected by having the developers and reference laboratory analyze extract duplicates. Extract duplicates were prepared by extracting a soil sample once and collecting two aliquots of the extract. For environmental samples, one sample from each depth interval was designated as an extract duplicate. Each sample designated as an extract duplicate was collected from a location where field triplicates were collected. To evaluate a given field measurement device's ability to precisely measure TPH, the relative standard deviation (RSD) of the device and reference method TPH results for triplicate samples was calculated. In addition, to evaluate the analytical precision of the device and reference method, the relative percent difference (RPD) was calculated using the TPH results for extract duplicates.

Primary Objective P3: Effect of Interferents

To evaluate the effect of interferents on each field measurement device's ability to accurately measure TPH, high-concentration-range soil PE samples containing weathered gasoline or diesel with or without an interferent were analyzed. As explained in Chapter 1, the definition of TPH is quite variable. For the purposes of addressing

primary objective P3, the term "interferent" is used in a broad sense and is applied to both PHC and non-PHC compounds. The six different interferents evaluated during the demonstration were MTBE; tetrachloroethene (PCE); Stoddard solvent; turpentine (an alpha and beta pinene mixture); 1,2,4-trichlorobenzene; and humic acid. The boiling points and vapor pressures of (1) MTBE and PCE are similar to those of GRO; (2) Stoddard solvent and turpentine are similar to those of GRO and EDRO; and (3) 1,2,4-trichlorobenzene and humic acid are similar to those of EDRO. The solubility, availability, and cost of the interferents were also considered during interferent selection. Specific reasons for the selection of the six interferents are presented below.

- MTBE is an oxygenated gasoline additive that is detected in the GRO analysis during TPH measurement using a GC.

- PCE is not a petroleum product but is detected in the GRO analysis during TPH measurement using a GC. PCE may also be viewed as a typical halogenated solvent that may be present in some environmental samples.

- Stoddard solvent is an aliphatic naphtha compound with a carbon range of n-C_8 through n-C_{14} and is partly detected in both the GRO and EDRO analyses during TPH measurement using a GC.

- Turpentine is not a petroleum product but has a carbon range of n-C_9 through n-C_{15} and is partly detected in both the GRO and EDRO analyses during TPH measurement using a GC. Turpentine may also be viewed as a substance that behaves similarly to a typical naturally occurring oil or grease during TPH measurement using a GC.

- The compound 1,2,4-trichlorobenzene is not a petroleum product but is detected in the EDRO analysis. This compound may also be viewed as a typical halogenated semivolatile organic compound that behaves similarly to a chlorinated pesticide or PCB during TPH measurement using a GC.

- Humic acid is a hydrocarbon mixture that is representative of naturally occurring organic carbon in soil and was suspected to be detected during EDRO analysis.

Based on the principles of operation of the field measurement devices, several of the interferents were suspected to be detected by the devices.

The PE samples containing MTBE and PCE were not prepared with diesel and the PE samples containing 1,2,4-trichlorobenzene and humic acid were not prepared with weathered gasoline because these interferents were not expected to impact the analyses and because practical difficulties such as solubility constraints were associated with preparation of such samples.

Appropriate control samples were also prepared and analyzed to address primary objective P3. These samples included processed garden soil, processed garden soil and weathered gasoline, processed garden soil and diesel, and processed garden soil and humic acid samples. Because of solubility constraints, control samples containing MTBE; PCE; Stoddard solvent; turpentine; or 1,2,4-trichlorobenzene could not be prepared. Instead, neat (liquid) samples of these interferents were prepared and used as quasi-control samples to evaluate the effect of each interferent on the field measurement device and reference method results. Each PE sample was prepared in triplicate and submitted to the developers and reference laboratory as blind triplicate samples.

To evaluate the effects of interferents on a given field measurement device's ability to accurately measure TPH under primary objective P3, the means and standard deviations of the TPH results for triplicate PE samples were calculated. The mean for each group of samples was qualitatively evaluated to determine whether the data showed any trend—that is, whether an increase in the interferent concentration resulted in an increase or decrease in the measured TPH concentration. A one-way analysis of variance was performed to determine whether the group means were the same or different.

Primary Objective P4: Effect of Soil Moisture Content

To evaluate the effect of soil moisture content, high-concentration-range soil PE samples containing weathered gasoline or diesel were analyzed. PE samples containing weathered gasoline were prepared at two moisture levels: 9 percent moisture and 16 percent moisture. PE samples containing diesel were also prepared at two moisture levels: negligible moisture (less than 1 percent) and 9 percent moisture. All the moisture levels were selected

based on the constraints associated with sample preparation. For example, 9 percent moisture represents the minimum moisture level for containerizing samples in EnCores and 16 percent moisture represents the saturation level of the soil used to prepare PE samples. Diesel samples with negligible moisture could be prepared because they did not require EnCores for containerization; based on vapor pressure data for diesel and weathered gasoline, 4-ounce jars were considered to be appropriate for containerizing diesel samples but not for containerizing weathered gasoline samples. Each PE sample was prepared in triplicate.

To measure the effect of soil moisture content on a given field measurement device's ability to accurately measure TPH under primary objective P4, the means and standard deviations of the TPH results for triplicate PE samples containing weathered gasoline and diesel at two moisture levels were calculated. A two-tailed, two-sample Student's t-test was performed to determine whether the device and reference method results were impacted by moisture—that is, to determine whether an increase in moisture resulted in an increase or decrease in the TPH concentrations measured.

Primary Objective P5: Time Required for TPH Measurement

The sample throughput (the number of TPH measurements per unit of time) was determined for each field measurement device by measuring the time required for each activity associated with TPH measurement, including device setup, sample extraction, sample analysis, and data package preparation. The EPA provided each developer with investigative samples stored in coolers. The developer unpacked the coolers and checked the chain-of-custody forms to verify that it had received the correct samples. Time measurement began when the developer began to set up its device. The total time required to complete analysis of all investigative samples was recorded. Analysis was considered to be complete and time measurement stopped when the developer provided the EPA with a summary table of results, a run log, and any supplementary information that the developer chose. The summary table listed all samples analyzed and their respective TPH concentrations.

For the reference laboratory, the total analytical time began to be measured when the laboratory received all the investigative samples, and time measurement continued until the EPA representatives received a complete data package from the laboratory.

Primary Objective P6: Costs Associated with TPH Measurement

To estimate the costs associated with TPH measurement for each field measurement device, the following five cost categories were identified: capital equipment, supplies, support equipment, labor, and investigation-derived waste (IDW) disposal. Chapter 8 of this ITVR discusses the costs estimated for the PetroFLAG™ System based on these cost categories.

Table 4-2 summarizes the demonstration approach used to address the primary objectives and includes demonstration area characteristics, approximate sampling depth intervals, and the rationale for the analyses performed by the reference laboratory.

4.2.2 Approach for Addressing Secondary Objectives

Secondary objectives were addressed based on field observations made during the demonstration. Specifically, EPA representatives observed TPH measurement activities and documented them in a field logbook. Each developer was given the opportunity to review the field logbook at the end of each day of the demonstration. The approach used to address each secondary objective for each field measurement device is discussed below.

- The skills and training required for proper device operation (secondary objective S1) were evaluated by observing and noting the skills required to operate the device and prepare the data package during the demonstration and by discussing necessary user training with developer personnel.

- Health and safety concerns associated with device operation (secondary objective S2) were evaluated by observing and noting possible health and safety concerns during the demonstration, such as the types of hazardous substances handled by developer personnel during analysis, the number of times that hazardous substances were transferred from one container to another during the analytical procedure, and direct exposure of developer personnel to hazardous substances.

Table 4-2. Demonstration Approach

Site	Area	Approximate Sampling Depth Interval (foot bgs)	Objective Addressed[a]	Soil Characteristics	Contamination Type	Typical TPH Concentration Range[b]	Rationale for Analyses by Reference Laboratory
Navy BVC	FFA	Upper layer[c]	P2	Medium-grained sand	Weathered diesel with carbon range from n-C_{10} through n-C_{40}	Low	Only EDRO because samples did not contain PHCs in gasoline range
		Lower layer[c]				High	
	NEX Service Station Area	7 to 8		Medium-grained sand	Fairly weathered gasoline with carbon range from n-C_6 through n-C_{14}	Low to medium	GRO and EDRO because samples contained PHCs in both gasoline and diesel ranges
		8 to 9				Medium to high	
		9 to 10				High	
		10 to 11				Low	
	PRA[d]	1.5 to 2.5		Silty sand	Heavy lubricating oil with carbon range from n-C_{14} through n-C_{40}	High	Only EDRO because samples did not contain PHCs in gasoline range
Kelly AFB	B-38 Area	23 to 25		Sandy clay or silty sand and gravel in upper depth interval and clayey sand and gravel in deeper depth interval	Fresh gasoline and diesel or weathered gasoline and trace amounts of lubricating oil with carbon range from n-C_6 through n-C_{40}	Low	GRO and EDRO because samples contained PHCs in both gasoline and diesel ranges
		25 to 27					
PC	SFT Area	2 to 4		Silty clay with traces of sand in deeper depth intervals	Combination of slightly weathered gasoline, kerosene, JP-5, and diesel with carbon range from n-C_5 through n-C_{32}	Medium	
		4 to 6					
		6 to 8					
		8 to 10					

Sample Matrix	Objective Addressed[a]	Soil Characteristics	Contamination Type	Typical TPH Concentration range[b]	Rationale for Analyses by Reference Laboratory
Ottawa sand (PE sample)	P1, P2	Fine-grained sand	Weathered gasoline[e,f]	Low	GRO and EDRO because weathered gasoline contains significant amounts of PHCs in both gasoline and diesel ranges
			Diesel		Only EDRO because diesel does not contain PHCs in gasoline range
Processed garden soil (PE sample)	P2	Silty sand	Weathered gasoline[e]	Medium and high	GRO and EDRO because weathered gasoline contains significant amounts of PHCs in both gasoline and diesel ranges
			Diesel		Only EDRO because diesel does not contain PHCs in gasoline range

Table 4-2. Demonstration Approach (Continued)

Sample Matrix	Objective Addressed[a]	Soil Characteristics	Contamination Type	Typical TPH Concentration range[b]	Rationale for Analyses by Reference Laboratory
Not applicable (neat liquid PE sample)	P2 (Continued)	Not applicable	Weathered gasoline	High	GRO and EDRO because weathered gasoline contains significant amounts of PHCs in both gasoline and diesel ranges
			Diesel	High	Only EDRO because diesel does not contain PHCs in gasoline range
Processed garden soil (PE sample)	P3	Silty sand	Blank soil (control sample)	Trace	GRO and EDRO because processed garden soil may contain trace concentrations of PHCs in both gasoline and diesel ranges
			Weathered gasoline	High	GRO and EDRO because weathered gasoline contains significant amounts of PHCs in both gasoline and diesel ranges
			Weathered gasoline and MTBE (1,100 mg/kg), PCE (2,810 mg/kg), Stoddard solvent (2,900 mg/kg), or turpentine (2,730 mg/kg)		
			Weathered gasoline and MTBE (1,700 mg/kg), PCE (13,100 mg/kg), Stoddard solvent (15,400 mg/kg), or turpentine (12,900 mg/kg)		
			Diesel		Only EDRO because diesel does not contain PHCs in gasoline range
			Diesel and Stoddard solvent (3,650 mg/kg) or turpentine (3,850 mg/kg)		GRO and EDRO because (1) Stoddard solvent contains PHCs in both gasoline and diesel ranges and (2) turpentine interferes with both analyses
			Diesel and Stoddard solvent (18,200 mg/kg) or turpentine (19,600 mg/kg)		
			Diesel and 1,2,4-trichlorobenzene (3,350 mg/kg) or humic acid (3,940 mg/kg)		Only EDRO because 1,2,4-trichloro-benzene and humic acid do not interfere with GRO analysis
			Diesel and 1,2,4-trichlorobenzene (16,600 mg/kg) or humic acid (19,500 mg/kg)		
			Humic acid (3,940 mg/kg)	Trace	Only EDRO because humic acid does not interfere with GRO analysis The contribution of trace concentrations (less than 15 mg/kg) GRO found in processed garden soil during the predemonstration investigation was considered to be insignificant evaluation of the effect of humic acid interference, which occurs in the diesel range.
			Humic acid (19,500 mg/kg)		

Table 4-2. Demonstration Approach (Continued)

Sample Matrix	Objective Addressed[a]	Soil Characteristics	Contamination Type	Typical TPH Concentration range[b]	Rationale for Analyses by Reference Laboratory
Not applicable (neat liquid PE sample)	P3 (Continued)	Not applicable	Weathered gasoline	High	GRO and EDRO because weathered gasoline contains significant amounts of PHCs in both gasoline and diesel ranges
			Diesel		Only EDRO because diesel does not contain PHCs in gasoline range
			MTBE		Only GRO because MTBE and PCE do not interfere with EDRO analysis
			PCE	Not applicable	
			Stoddard solvent	High	GRO and EDRO because Stoddard solvent contains PHCs in both gasoline and diesel ranges
			Turpentine	Not applicable	GRO and EDRO because turpentine interferes with both analyses
			1,2,4-Trichlorobenzene		Only EDRO because 1,2,4-trichloro-benzene does not interfere with GRO analysis
Processed garden soil (PE sample)	P4	Silty sand	Weathered gasoline (samples prepared at 9 and 16 percent moisture levels)	High	GRO and EDRO because weathered gasoline contains significant amounts of PHCs in both gasoline and diesel ranges
			Diesel (samples prepared at negligible [less than 1 percent] and 9 percent moisture levels)		Only EDRO because diesel does not contain PHCs in gasoline range

Notes:

AFB = Air Force Base
bgs = Below ground surface
BVC = Base Ventura County
FFA = Fuel Farm Area
mg/kg = Milligram per kilogram
MTBE = Methyl-tert-butyl ether
NEX = Naval Exchange
PC = Petroleum company
PCE = Tetrachloroethene
PE = Performance evaluation
PHC = Petroleum hydrocarbon
PRA = Phytoremediation Area
SFT = Slop Fill Tank

[a] Field observations of all sample analyses conducted during the demonstration were used to address primary objectives P5 and P6 and the secondary objectives.

[b] The typical TPH concentration range was based on reference laboratory results for the demonstration. The typical low, medium, and high ranges indicate TPH concentrations of less than 100 mg/kg; 100 to 1,000 mg/kg; and greater than 1,000 mg/kg, respectively.

[c] Because of soil conditions encountered in the FFA during the demonstration, the sampling depth intervals could not be accurately determined. Sample collection was initiated approximately 10 feet bgs, and attempts were made to collect 4-foot-long soil cores. For each sampling location in the area, the sample cores were divided into two samples based on visual observations. The upper layer of the soil core made up one sample, and the lower layer of the soil core made up the second sample.

[d] Dexsil chose not to analyze soil samples collected in the PRA because Dexsil believed that the natural organic material in the area would adversely impact the PetroFLAG™ System's ability to accurately measure TPH.

Table 4-2. Demonstration Approach (Continued)

[e] Dexsil chose not to analyze low- and medium-concentration-range weathered gasoline soil PE samples because according to Dexsil, the PetroFLAG™ System was not sensitive to weathered gasoline concentrations of less than 1,000 mg/kg.

[f] Because of problems that arose during preparation of PE samples with low concentrations of weathered gasoline, the results for these samples were not used to evaluate the field measurement devices.

- The portability of the device (secondary objective S3) was evaluated by observing and noting the weight and size of the device and additional equipment required for TPH measurement as well as how easily the device was set up for use during the demonstration.

- The durability of the device (secondary objective S4) was evaluated by noting the materials of construction of the device and additional equipment required for TPH measurement. In addition, EPA representatives noted likely device failures or repairs that may be necessary during extended use of the device. Downtime required to make device repairs during the demonstration was also noted.

- The availability of the device and associated spare parts (secondary objective S5) was evaluated by discussing the availability of replacement devices with developer personnel and determining whether spare parts were available in retail stores or only from the developer. In addition, the availability of spare parts required during the demonstration was noted.

Field observations of the analyses of all the samples described in Table 4-2 were used to address the secondary objectives for the demonstration.

4.3 Sample Preparation and Management

This section presents sample preparation and management procedures used during the demonstration. Specifically, this section describes how samples were collected, containerized, labeled, stored, and shipped during the demonstration. Additional details about the sample preparation and management procedures are presented in the demonstration plan (EPA 2000).

4.3.1 Sample Preparation

The sample preparation procedures for both environmental and PE samples are described below.

Environmental Samples

For the demonstration, environmental samples were collected in the areas that were used for the predemonstration investigation: (1) the FFA and NEX Service Station Area at the Navy BVC site; (2) the B-38 Area at the Kelly AFB site; and (3) the SFT Area at the PC site. Samples were collected in all areas using a Geoprobe®.

The liners containing environmental samples were transported to the sample management trailer at the Navy BVC site, where the liners were cut open longitudinally. A geologist then profiled the samples based on soil characteristics to determine where the soil cores had to be sectioned. The soil characterization performed for each demonstration area is summarized in Chapter 3.

Each core sample section was then transferred to a stainless-steel bowl. The presence of any unrepresentative material such as sticks, roots, and stones was noted in a field logbook, and such material was removed to the extent possible using gloved hands. Any lump of clay in the sample that was greater than about 1/8 inch in diameter was crushed between gloved fingers before homogenization. Each soil sample was homogenized by stirring it for at least 2 minutes using a stainless-steel spoon or gloved hands until the sample was visibly homogeneous. During or immediately following homogenization, any free water was poured from the stainless-steel bowl containing the soil sample into a container designated for IDW. During the demonstration, the field sampling team used only nitrile gloves to avoid the possibility of phthalate contamination from handling samples with plastic gloves. Such contamination had occurred during the predemonstration investigation.

After sample homogenization, the samples were placed in (1) EnCores of approximately 5-gram capacity for GRO analysis; (2) 4-ounce, glass jars provided by the reference laboratory for EDRO and percent moisture analyses; and (3) EnCores of approximately 25-gram capacity for TPH analysis. Using a quartering technique, each sample container was filled by alternately spooning soil from one quadrant of the mixing bowl and then from the opposite quadrant until the container was full. The 4-ounce, glass jars were filled after all the EnCores for a given sample had been filled. After a sample container was filled, it was immediately closed to minimize volatilization of contaminants. To minimize the time required for sample homogenization and filling of sample containers, these activities were simultaneously conducted by four personnel.

Because of the large number of containers being filled, some time elapsed between the filling of the first EnCore and the filling of the last. An attempt was made to

eliminate any bias by alternating between filling EnCores for the developers and filling EnCores for the reference laboratory. Table 4-3 summarizes the demonstration sampling depth intervals, numbers of environmental and QA/QC samples collected, and numbers of environmental sample analyses associated with the demonstration of the PetroFLAG™ System.

Performance Evaluation Samples

All PE samples for the demonstration were prepared by ERA and shipped to the sample management trailer at the Navy BVC site. PE samples consisted of both soil samples and liquid samples. ERA prepared soil PE samples using two soil matrixes: Ottawa sand and processed garden soil (silty sand).

To prepare the soil PE samples, ERA spiked the required volume of soil based on the number of PE samples and the quantity of soil per PE sample requested. ERA then homogenized the soil by manually mixing it. ERA used weathered gasoline or diesel as the spiking material, and spiking was done at three levels to depict the three TPH concentration ranges: low, medium, and high. A low-range sample was spiked to correspond to a TPH concentration of less than 100 mg/kg; a medium-range sample was spiked to correspond to a TPH concentration range of 100 to 1,000 mg/kg; and a high-range sample was spiked to correspond to a TPH concentration of more than 1,000 mg/kg.

To spike each low- and medium-range soil sample, ERA used methanol as a "carrier" to distribute the contaminant

Table 4-3. Environmental Samples

Site	Area	Depth Interval (foot bgs)	Number of Sampling Locations	Total Number of Samples, Including Field Triplicates, to Dexsil and Reference Laboratory[a]	Number of MS/MSD[b] Pairs	Number of Extract Duplicates[c]	Number of TPH Analyses by Dexsil	Number of Analyses by Reference Laboratory[d]	
								GRO	EDRO
Navy BVC	FFA	Upper layer	3	5	1	1	6	0	8
		Lower layer	3	5	1	1	6	0	8
	NEX Service Station Area	7 to 8	3	5	1	1	6	8	8
		8 to 9	3	5	1	1	6	8	8
		9 to 10	3	5	1	1	6	8	8
		10 to 11	3	5	1	1	6	8	8
Kelly AFB	B-38 Area	23 to 25	3	5	1	1	6	8	8
		25 to 27	3	3	1	1	4	6	6
PC	SFT Area	2 to 4	5	7	1	1	8	10	10
		4 to 6	5	7	1	1	8	10	10
		6 to 8	5	7	1	1	8	10	10
		8 to 10	5	7	1	1	8	10	10
Total				**66**	**12**	**12**	**78**	**86**	**102**

Notes:

AFB = Air Force Base
bgs = Below ground surface
BVC = Base Ventura County
FFA = Fuel Farm Area
MS/MSD = Matrix spike and matrix spike duplicate
NEX = Naval Exchange
PC = Petroleum company
SFT = Slop Fill Tank

[a] Field triplicates were collected at a frequency of one per depth interval in each sampling area except the B-38 Area. Because of conditions in the B-38 Area, triplicates were collected in the top depth interval only. Three separate, blind samples were prepared for each field triplicate.

[b] MS/MSD samples were collected at a frequency of one per depth interval in each sampling area for analysis by the reference laboratory. MS/MSD samples were not analyzed by Dexsil.

[c] Because of site conditions, Dexsil did not analyze extract duplicates for the upper clay layer in the FFA and the 10- to 11-foot bgs depth interval in the NEX Service Station Area.

[d] All environmental samples were also analyzed for moisture content by the reference laboratory.

evenly throughout the sample. Soil PE samples were spiked with interferents at two different levels ranging from 50 to 500 percent of the TPH concentration expected to be present. Whenever possible, the interferents were added at levels that best represented real-world conditions. ERA analyzed the samples containing weathered gasoline before shipping them to the Navy BVC site. The analytical results were used to confirm sample concentrations.

Liquid PE samples consisted of neat materials. Each liquid PE sample consisted of approximately 2 mL of liquid in a flame-sealed, glass ampule. During the demonstration, the developers and reference laboratory were given a table informing them of the amount of liquid sample to be used for analysis.

ERA grouped like PE samples together in a resealable bag and placed all the PE samples in a cooler containing ice for overnight shipment to the Navy BVC site. When the PE samples arrived at the site, the samples were labeled with the appropriate sample identification numbers and placed in appropriate coolers for transfer to the developers on site or for shipment to the reference laboratory as summarized in Section 4.3.2. Table 4-4 summarizes the contaminant types and concentration ranges as well as the numbers of PE samples and analyses associated with the demonstration of the PetroFLAG™ System.

4.3.2 Sample Management

Following sample containerization, each environmental sample was assigned a unique sample designation defining the sampling area, expected type of contamination, expected concentration range, sampling location, sample number, and QC identification, as appropriate. Each sample container was labeled with the unique sample designation, date, time, preservative, initials of personnel who had filled the container, and analysis to be performed. Each PE sample was also assigned a unique sample designation that identified it as a PE sample. Each PE sample designation also identified the expected contaminant type and range, whether the sample was soil or liquid, and the sample number.

Sample custody began when samples were placed in iced coolers in the possession of the designated field sample custodian. Demonstration samples were divided into two groups to allow adequate time for the developers and reference laboratory to extract and analyze samples within the method-specified holding times presented in Table 4-5. The two groups of samples for reference laboratory analysis were placed in coolers containing ice and chain-of-custody forms and were shipped by overnight courier to the reference laboratory on the first and third days of the demonstration. The two groups of samples for developer analysis were placed in coolers containing ice and chain-of-custody forms and were hand-delivered to the developers at the Navy BVC site on the same days that the reference laboratory received its two groups of samples. During the demonstration, each developer was provided with a tent to provide shelter from direct sunlight during analysis of demonstration samples. In addition, at the end of each day, the developer placed any samples or sample extracts in its custody in coolers, and the coolers were stored in a refrigerated truck.

Table 4-4. Performance Evaluation Samples

Sample Type	Typical TPH Concentration Range[a]	Total Number of Samples to Dexsil and Reference Laboratory	Number of MS/MSD[b] Pairs	Number of Analyses by Dexsil	Number of Analyses by Reference Laboratory[c]	
					GRO	EDRO
Soil Samples (Ottawa Sand)						
Weathered gasoline	Low	7	0	0[d]	7	7
Diesel		7	0	7	0	7
Soil Samples (Processed Garden Soil)						
Weathered gasoline	Medium	3	0	0[d]	3	3
	High	3	1	3	5	5
Diesel	Medium	3	0	3	0	3
	High	3	1	3	0	5
Blank soil (control sample)	Trace	3	1	3	5	5
MTBE (1,100 mg/kg) and weathered gasoline	High	3	0	3	3	3
MTBE (1,700 mg/kg) and weathered gasoline		3	0	3	3	3
PCE (2,810 mg/kg) and weathered gasoline		3	0	3	3	3
PCE (13,100 mg/kg) and weathered gasoline		3	0	3	3	3
Stoddard solvent (2,900 mg/kg) and weathered gasoline		3	0	3	3	3
Stoddard solvent (15,400 mg/kg) and weathered gasoline		3	0	3	3	3
Turpentine (2,730 mg/kg) and weathered gasoline		3	0	3	3	3
Turpentine (12,900 mg/kg) and weathered gasoline		3	0	3	3	3
Stoddard solvent (3,650 mg/kg) and diesel		3	0	3	3	3
Stoddard solvent (18,200 mg/kg) and diesel		3	0	3	3	3
Turpentine (3,850 mg/kg) and diesel		3	0	3	3	3
Turpentine (19,600 mg/kg) and diesel		3	0	3	3	3
1,2,4-Trichlorobenzene (3,350 mg/kg) and diesel		3	0	3	0	3
1,2,4-Trichlorobenzene (16,600 mg/kg) and diesel		3	0	3	0	3
Humic acid (3,940 mg/kg) and diesel		3	0	3	0	3
Humic acid (19,500 mg/kg) and diesel		3	0	3	0	3
Humic acid (3,940 mg/kg)	Trace	3	0	3	0	3
Humic acid (19,500 mg/kg)		3	0	3	0	3
Weathered gasoline at 16 percent moisture	High	3	1	3	5	5
Diesel at negligible moisture (less than 1 percent)		3	1	3	0	5
Liquid Samples (Neat Material)						
Weathered gasoline	High	3	1	3	5	5
Diesel		3	0	3	0	3
MTBE		6	0	6	6	0

Table 4-4. Performance Evaluation Samples (Continued)

Sample Type	Typical TPH Concentration Range[a]	Total Number of Samples to Dexsil and Reference Laboratory	Number of MS/MSD[b] Pairs	Number of Analyses by Dexsil	Number of Analyses by Reference Laboratory[c]	
					GRO	EDRO
Liquid Samples (Neat Material) (Continued)						
PCE	Not applicable	6	0	6	6	0
Stoddard solvent	High	6	0	6	6	6
Turpentine	Not applicable	6	0	6	6	6
1,2,4-Trichlorobenzene		6	0	6	0	6
Total		**125**	**6**	**115**	**90**	**125**

Notes:

mg/kg = Milligram per kilogram
MS/MSD = Matrix spike and matrix spike duplicate
MTBE = Methyl-tert-butyl ether
PCE = Tetrachloroethene

[a] The typical TPH concentration range was based on reference laboratory results for the demonstration. The typical low, medium, and high ranges indicate TPH concentrations of less than 100 mg/kg; 100 to 1,000 mg/kg; and greater than 1,000 mg/kg, respectively. The typical TPH concentration range for the liquid sample concentrations was based on the definition of TPH used for the demonstration and knowledge of the sample (neat material).

[b] MS/MSD samples were analyzed only by the reference laboratory.

[c] All soil performance evaluation samples were also analyzed for moisture content by the reference laboratory.

[d] Dexsil chose not to analyze low- and medium-concentration-range weathered gasoline soil performance evaluation samples because according to Dexsil, the PetroFLAG™ System was not sensitive to weathered gasoline concentrations of less than 1,000 mg/kg.

Table 4-5. Sample Container, Preservation, and Holding Time Requirements

Parameter[a]	Medium	Container	Preservation	Holding Time (days)	
				Extraction	Analysis
GRO	Soil	Two 5-gram EnCores	4 ± 2 °C	2[b]	14
EDRO	Soil	Two 4-ounce, glass jars with Teflon™-lined lids	4 ± 2 °C	14[b]	40
Percent moisture	Soil	Two 4-ounce, glass jars with Teflon™-lined lids	4 ± 2 °C	Not applicable	7
TPH	Soil	One 25-gram EnCore	4 ± 2 °C	Performed on site[c]	
GRO and EDRO	Liquid	One 2-milliliter ampule for each analysis	Not applicable	See note d	

Notes:

± = Plus or minus

[a] The reference laboratory measured percent moisture using part of the soil sample from the container designated for EDRO analysis.

[b] The extraction holding time started on the day that samples were shipped.

[c] If GRO analysis of a sample was to be completed by the reference laboratory, the developers completed on-site extraction of the corresponding sample within 2 days. Otherwise, all on-site extractions and analyses were completed within 7 days.

[d] The reference laboratory cracked open each ampule and immediately added the specified aliquot of the sample to methanol for GRO analysis and to methylene chloride for EDRO analysis. This procedure was performed in such a way that the final volumes of the extracts for GRO and EDRO analyses were 5.0 milliliters and 1.0 milliliter, respectively. Once the extracts were prepared, the GRO and EDRO analyses were performed within 14 and 40 days, respectively.

Chapter 5
Confirmatory Process

The performance results for each field measurement device were compared to those for an off-site laboratory measurement method—that is, a reference method. This chapter describes the rationale for the selection of the reference method (Section 5.1) and reference laboratory (Section 5.2) and summarizes project-specific sample preparation and analysis procedures associated with the reference method (Section 5.3).

5.1 Reference Method Selection

During the demonstration, environmental and PE samples were analyzed for TPH by the reference laboratory using SW-846 Method 8015B (modified). This section describes the analytical methods considered for the demonstration and provides a rationale for the reference method selected.

The reference method used was selected based on the following criteria:

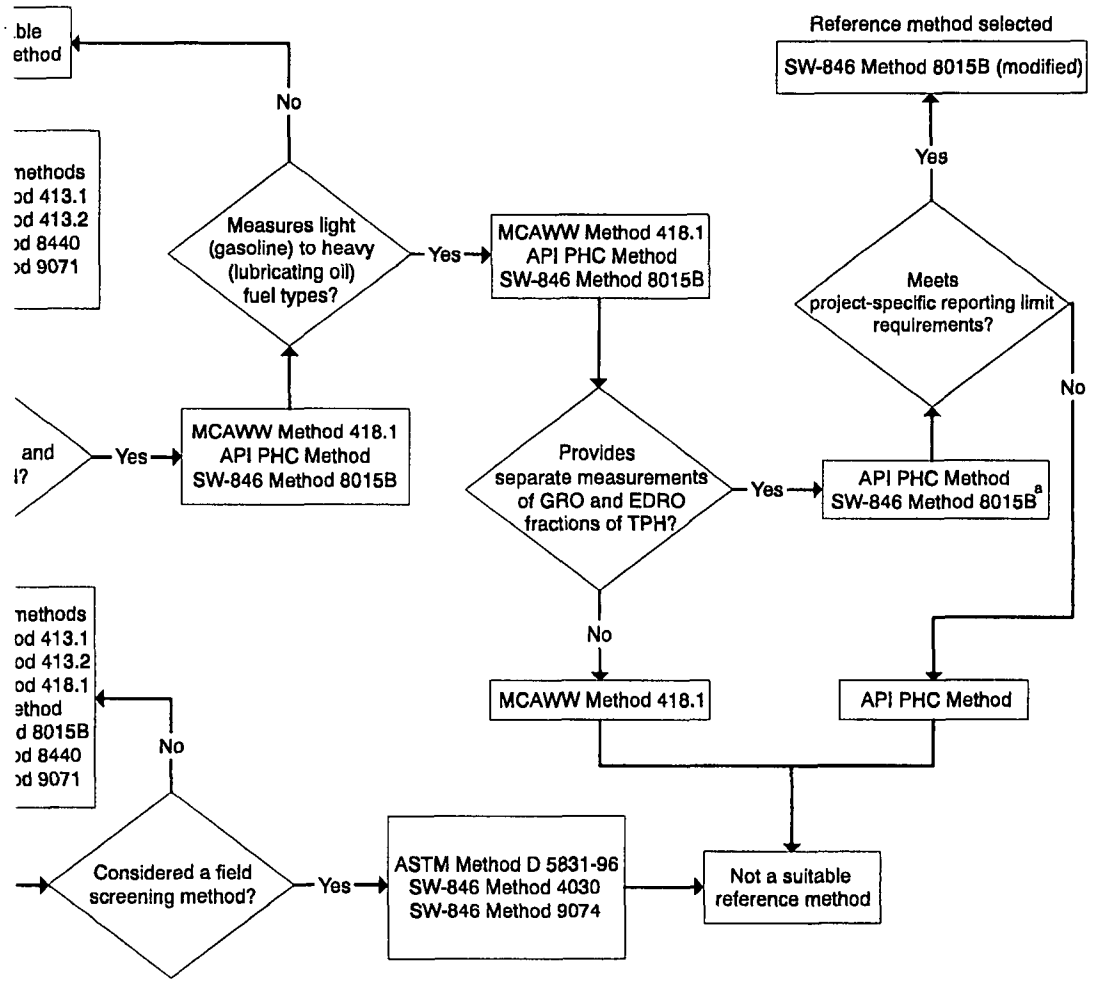
- It is not a field screening method.
- It is widely used and accepted.
- It measures light (gasoline) to heavy (lubricating oil) fuel types.
- It can provide separate measurements of GRO and EDRO fractions of TPH.
- It meets project-specific reporting limit requirements.

The analytical methods considered for the demonstration and the reference method selected based on the above-listed criteria are illustrated in a flow diagram in Figure 5-1. The reference method selection process is discussed below.

Analytical methods considered for the demonstration were identified based on a review of SW-846, "Methods for Chemical Analysis of Water and Wastes" (MCAWW), ASTM, API, and state-specific methods. The analytical methods considered collectively represent six different measurement technologies. Of the methods reviewed, those identified as field screening methods, such as SW-846 Method 4030, were eliminated from further consideration in the reference method selection process.

A literature review was conducted to determine whether the remaining methods are widely used and accepted in the United States (Association for the Environmental Health of Soil [AEHS] 1999). As a result of this review, state-specific methods such as the Massachusetts Extractable Petroleum Hydrocarbon (EPH) and Volatile Petroleum Hydrocarbon (VPH) Methods (Massachusetts Department of Environmental Protection 2000), the Florida Petroleum Range Organic (PRO) Method (Florida Department of Environmental Protection 1996), and Texas Method 1005 (Texas Natural Resource Conservation Commission 2000) were eliminated from the selection process. Also eliminated were the gravimetric and infrared methods except for MCAWW Method 418.1 (EPA 1983). The use and acceptability of MCAWW Method 418.1 will likely decline because the extraction solvent used in this method is Freon 113, a chlorofluorocarbon (CFC), and use of CFCs will eventually be phased out under the Montreal Protocol. However, because several states still accept the use of MCAWW Method 418.1 for measuring TPH, the method was retained for further consideration in the selection process (AEHS 1999).

Of the remaining methods, MCAWW Method 418.1, the API PHC Method, and SW-846 Method 8015B can all measure light (gasoline) to heavy (lubricating oil) fuel types. However, GRO and EDRO fractions cannot be



or Testing and Materials, DRO = diesel range organics, EPH = extractable petroleum hydrocarbon, GC/FID = gas chromatograph/flame
s of Water and Wastes," PHC = petroleum hydrocarbon, PRO = petroleum range organics, SW-846 = "Test Methods for Evaluating

measurements and, when modified, can also provide EDRO measurements.

measured separately using MCAWW Method 418.1. As a result, this method was eliminated from the selection process.

Both the API PHC Method and SW-846 Method 8015B can be used to separately measure the GRO and DRO fractions of TPH. These methods can also be modified to extend the DRO range to EDRO by using a calibration standard that includes even-numbered alkanes in the EDRO range.

Based on a review of state-specific action levels for TPH, a TPH reporting limit of 10 mg/kg was used for the demonstration. Because the TPH reporting limit for the API PHC Method (50 to 100 mg/kg) is greater than 10 mg/kg, this method was eliminated from the selection process (API 1994). SW-846 Method 8015B (modified) met the reporting limit requirements for the demonstration. For GRO, SW-846 Method 8015B (modified) has a reporting limit of 5 mg/kg, and for EDRO, this method has a reporting limit of 10 mg/kg. Therefore, SW-846 Method 8015B (modified) satisfied all the criteria established for selecting the reference method. As an added benefit, because this is a GC method, it also provides a fingerprint (chromatogram) of TPH components.

5.2 Reference Laboratory Selection

This section provides the rationale for the selection of the reference laboratory. STL Tampa East was selected as the reference laboratory because it (1) has been performing TPH analyses for many years, (2) has passed many external audits by successfully implementing a variety of TPH analytical methods, and (3) agreed to implement project-specific analytical requirements. In January 2000, a project-specific audit of the laboratory was conducted and determined that STL Tampa East satisfactorily implemented the reference method during the predemonstration investigation. In addition, STL Tampa East successfully analyzed double-blind PE samples and blind field triplicates for GRO and EDRO during the predemonstration investigation. Furthermore, in 1998 STL Tampa East was one of four recipients and in 1999 was one of six recipients of the Seal of Excellence Award issued by the American Council of Independent Laboratories. In each instance, this award was issued based on the results of PE sample analyses and client satisfaction surveys. Thus, the selection of the reference laboratory was based primarily on performance and not cost.

5.3 Summary of Reference Method

The laboratory sample preparation and analytical methods used for the demonstration are summarized in Table 5-1. The SW-846 methods listed in Table 5-1 for GRO and EDRO analyses were tailored to meet the definition of TPH for the project (see Chapter 1). Project-specific procedures for soil sample preparation and analysis for GRO and EDRO are summarized in Tables 5-2 and 5-3, respectively. Project-specific procedures were applied

Table 5-1. Laboratory Sample Preparation and Analytical Methods

Parameter	Method Reference (Step)	Method Title
GRO	Based on SW-846 Method 5035 (extraction)	Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples
	Based on SW-846 Method 5030B (purge-and-trap)	Purge-and-Trap for Aqueous Samples
	Based on SW-846 Method 8015B (analysis)	Nonhalogenated Volatile Organics by Gas Chromatography
EDRO	Based on SW-846 Method 3540C (extraction)	Soxhlet Extraction
	Based on SW-846 Method 8015B (analysis)	Nonhalogenated Volatile Organics by Gas Chromatography
Percent moisture	Based on MCAWW Method 160.3[a]	Residue, Total (Gravimetric, Dried at 103-105 °C)

Notes:

MCAWW = "Methods for Chemical Analysis of Water and Wastes"
SW-846 = "Test Methods for Evaluating Solid Waste"

[a] MCAWW Method 160.3 was modified to include calculation and reporting of percent moisture in soil samples.

Table 5-2. Summary of Project-Specific Procedures for GRO Analysis

SW-846 Method Reference (Step)	Project-Specific Procedures
5035 (Extraction)	
Low-level (0.5 to 200 micrograms per kilogram) or high-level (greater than 200 micrograms per kilogram) samples may be prepared.	Because the project-specific reporting limit for GRO was 5 milligrams per kilogram, all samples analyzed for GRO were prepared using procedures for high-level samples.
Samples may be collected with or without use of a preservative solution.	Samples were collected without use of a preservative.
A variety of sample containers, including EnCores, may be used when high-level samples are collected without use of a preservative.	Samples were containerized in EnCores.
Samples collected in EnCores should be transferred to vials containing the extraction solvent as soon as possible or analyzed within 48 hours.	Samples were weighed and extracted within 2 calendar days of their shipment. The holding time for analysis was 14 days after extraction. A full set of quality control samples (method blanks, MS/MSDs, and LCS/LCSDs) was prepared within this time.
For samples not preserved in the field, a solubility test should be performed using methanol, polyethylene glycol, and hexadecane to determine an appropriate extraction solvent.	Because the reference laboratory obtained acceptable results for performance evaluation samples extracted with methanol during the predemonstration investigation, samples were extracted with methanol.
Removal of unrepresentative material from the sample is not discussed.	During sample homogenization, field sampling technicians attempted to remove unrepresentative material such as sticks, roots, and stones if present in the sample; the reference laboratory did not remove any remaining unrepresentative material.
Procedures for adding surrogates to the sample are inconsistently presented. Section 2.2.1 indicates that surrogates should be added to an aliquot of the extract solution. Section 7.3.3 indicates that soil should be added to a vial containing both the extraction solvent (methanol) and surrogate spiking solution.	The soil sample was ejected into a volatile organic analysis vial, an appropriate amount of surrogate solution was added to the sample, and then methanol was quickly added.
Nine mL of methanol should be added to a 5-gram (wet weight) soil sample.	Five mL of methanol was added to the entire soil sample contained in a 5-gram EnCore.
When practical, the sample should be dispersed to allow contact with the methanol by shaking or using other mechanical means for 2 min without opening the sample container. When shaking is not practical, the sample should be dispersed with a narrow, metal spatula, and the sample container should be immediately resealed.	The sample was dispersed using a stainless-steel spatula to allow contact with the methanol. The volatile organic analysis vial was then capped and shaken vigorously until the soil was dispersed in methanol, and the soil was allowed to settle.
5030B (Purge-and-Trap)	
Screening of samples before the purge-and-trap procedure is recommended using one of the two following techniques: Use of an automated headspace sampler (see SW-846 Method 5021) connected to a GC equipped with a photoionization detector in series with an electrolytic conductivity detector Extraction of the samples with hexadecane (see SW-846 Method 3820) and analysis of the extracts using a GC equipped with a flame ionization detector or electron capture detector	Samples were screened with an automated headspace sampler (see SW-846 Method 5021) connected to a GC equipped with a flame ionization detector.
SW-846 Method 5030B indicates that contamination by carryover can occur whenever high-level and low-level samples are analyzed in sequence. Where practical, analysis of samples with unusually high concentrations of analytes should be followed by an analysis of organic-free reagent water to check for cross-contamination. Because the trap and other parts of the system are subject to contamination, frequent bake-out and purging of the entire system may be required.	According to the reference laboratory, a sample extract concentration equivalent to 10,000 ng on-column is the minimum concentration of GRO that could result in carryover. Therefore, if a sample extract had a concentration that exceeded the minimum concentration for carryover, the next sample in the sequence was evaluated as follows: (1) if the sample was clean (had no chromatographic peaks), no carryover had occurred; (2) if the sample had detectable analyte concentrations (chromatographic peaks), it was reanalyzed under conditions in which carryover did not occur.

Table 5-2. Summary of Project-Specific Procedures for GRO Analysis (Continued)

SW-846 Method Reference (Step)	Project-Specific Procedures
5030B (Purge-and-Trap) (Continued)	
The sample purge device used must demonstrate adequate performance.	A Tekmar 2016 autosampler and a Tekmar LSC 2000 concentrator were used. Based on quality control sample results, the reference laboratory had demonstrated adequate performance using these devices.
Purge-and-trap conditions for high-level samples are not clearly specified. According to SW-846, manufacturer recommendations for the purge-and-trap devices should be considered when the method is implemented. The following general purge-and-trap conditions are recommended for samples that are water-miscible (methanol extract): Purge gas: nitrogen or helium Purge gas flow rate: 20 mL/min Purge time: 15 ± 0.1 min Purge temperature: 85 ± 2 °C Desorb time: 1.5 min Desorb temperature: 180 °C Backflush inert gas flow rate: 20 to 60 mL/min Bake time: not specified Bake temperature: not specified Multiport valve and transfer line temperatures: not specified	The purge-and-trap conditions that were used are listed below. These conditions were based on manufacturer recommendations for the purge device specified above and the VOCARB 3000 trap. Purge gas: helium Purge gas flow rate: 35 mL/min Purge time: 8 min with 2-min dry purge Purge temperature: ambient temperature Desorb time: 1 min Desorb temperature: 250 °C Backflush inert gas flow rate: 35 mL/min Bake time: 7 min Bake temperature: 270 °C Multiport valve and transfer line temperatures: 115 and 120 °C
8015B (Analysis)	
GC Conditions	
The following GC conditions are recommended: Column: 30-meter x 0.53-millimeter-inside diameter, fused-silica capillary column chemically bonded with 5 percent methyl silicone, 1.5-micrometer field thickness Carrier gas: helium Carrier gas flow rate: 5 to 7 mL/min Makeup gas: helium Makeup gas flow rate: 30 mL/min Injector temperature: 200 °C Detector temperature: 340 °C Temperature program: Initial temperature: 45 °C Hold time: 1 min Program rate: 45 to 100 °C at 5 °C/min Program rate: 100 to 275 °C at 8 °C/min Hold time: 5 min Overall time: 38.9 min	The HP 5890 Series II was used as the GC. The following GC conditions were used based on manufacturer recommendations: Column: 30-meter x 0.53-millimeter-inside diameter, fused-silica capillary column chemically bonded with 5 percent methyl silicone, 1.5-micrometer field thickness Carrier gas: helium Carrier gas flow rate: 15 mL/min Makeup gas: helium Makeup gas flow rate: 15 mL/min Injector temperature: 200 °C Detector temperature: 200 °C Temperature program: Initial temperature: 25 °C Hold time: 3 min Program rate: 25 to 120 °C at 25 °C/min Hold time: 4 min Program rate: 120 to 245 °C at 25 °C/min Hold time: 5 min Overall time: 20.4 min
Calibration	
The chromatographic system may be calibrated using either internal or external standards.	The chromatographic system was calibrated using external standards with a concentration range equivalent to 100 to 10,000 ng on-column. The reference laboratory acceptance criterion for initial calibration was a relative standard deviation less than or equal to 20 percent of the average response factor or a correlation coefficient for the least-squares linear regression greater than or equal to 0.990.
Calibration should be performed using samples of the specific fuel type contaminating the site. When such samples are not available, recently purchased, commercially available fuel should be used.	Calibration was performed using a commercially available, 10-component GRO standard that contained 35 percent aliphatic hydrocarbons and 65 percent aromatic hydrocarbons.

Table 5-2. Summary of Project-Specific Procedures for GRO Analysis (Continued)

SW-846 Method Reference (Step)	Project-Specific Procedures
8015B (Analysis) (Continued)	
Calibration (Continued)	
Initial calibration verification is not required.	Initial calibration verification was performed using a second-source standard that contained a 10-component GRO standard made up of 35 percent aliphatic hydrocarbons and 65 percent aromatic hydrocarbons at a concentration equivalent to 2,000 ng on-column. The reference laboratory acceptance criterion for initial calibration verification was an instrument response within 25 percent of the response obtained during initial calibration.
CCV should be performed at the beginning of every 12-hour work shift and at the end of an analytical sequence. CCV throughout the 12-hour shift is also recommended; however, the frequency is not specified.	CCV was performed at the beginning of each analytical batch, after every tenth analysis, and at the end of the analytical batch. The reference laboratory acceptance criteria for CCV were instrument responses within 25 percent (for the closing CCV) and 15 percent (for all other CCVs) of the response obtained during initial calibration.
CCV should be performed using a fuel standard.	CCV was performed using a commercially available, 10-component GRO standard that contained 35 percent aliphatic hydrocarbons and 65 percent aromatic hydrocarbons.
According to SW-846 Method 8000, CCV should be performed at the same concentration as the midpoint concentration of the initial calibration curve; however, the concentration of each calibration point is not specified.	CCV was performed at a concentration equivalent to 2,000 ng on-column.
A method sensitivity check is not required.	A method sensitivity check was performed daily using a calibration standard with a concentration equivalent to 100 ng on-column. The reference laboratory acceptance criterion for the method sensitivity check was detection of the standard.
Retention Time Windows	
The retention time range (window) should be established using 2-methylpentane and 1,2,4-trimethylbenzene during initial calibration. Three measurements should be made over a 72-hour period; the results should be used to determine the average retention time. As a minimum requirement, the retention time should be verified using a midlevel calibration standard at the beginning of each 12-hour shift. Additional analysis of the standard throughout the 12-hour shift is strongly recommended.	The retention time range was established using the opening CCV specific to each analytical batch. The first eluter, 2-methylpentane, and the last eluter, 1,2,4-trimethylbenzene, of the GRO standard were used to establish each day's retention time range.
Quantitation	
Quantitation is performed by summing the areas of all chromatographic peaks eluting within the retention time range established using 2-methylpentane and 1,2,4-trimethylbenzene. Subtraction of the baseline rise for the method blank resulting from column bleed is generally not required.	Quantitation was performed by summing the areas of all chromatographic peaks from 2-methylpentane through 1,2,4-trimethylbenzene. This range includes n-C_{10}. Baseline rise subtraction was not performed.
Quality Control	
Spiking compounds for MS/MSDs and LCSs are not specified.	The spiking compound mixture for MS/MSDs and LCSs was the 10-component GRO calibration standard.
According to SW-846 Method 8000, spiking levels for MS/MSDs are determined differently for compliance and noncompliance monitoring applications. For noncompliance applications, the laboratory may spike the sample (1) at the same concentration as the reference sample (LCS), (2) at 20 times the estimated quantitation limit for the matrix of interest, or (3) at a concentration near the middle of the calibration range.	MS/MSD spiking levels were targeted to be between 50 and 150 percent of the unspiked sample concentration. The reference laboratory used historical information to adjust spike amounts or to adjust sample amounts to a preset spike amount. The spiked samples and unspiked samples were prepared such that the sample mass and extract volume used for analysis were the same.

Table 5-2. Summary of Project-Specific Procedures for GRO Analysis (Continued)

SW-846 Method Reference (Step)	Project-Specific Procedures
8015B (Analysis) (Continued)	
Quality Control (Continued)	
According to SW-846 Method 8000, in-house laboratory acceptance criteria for MS/MSDs and LCSs should be established. As a general rule, the recoveries of most compounds spiked into a sample should fall within the range of 70 to 130 percent, and this range should be used as a guide in evaluating in-house performance.	The reference laboratory acceptance criteria for MS/MSDs and LCSs were a relative percent difference less than or equal to 25 with 33 to 115 percent recovery. The acceptance criteria were based on laboratory historical information. These acceptance criteria are similar to those of the methods cited in Figure 5-1.
The LCS should consist of an aliquot of a clean (control) matrix that is similar to the sample matrix.	The LCS/LCSD matrix was Ottawa sand.
No LCSD is required.	The spiking compound mixture for LCSDs was the 10-component GRO calibration standard.
The surrogate compound and spiking concentration are not specified. According to SW-846 Method 8000, in-house laboratory acceptance criteria for surrogate recoveries should be established.	The surrogate compound was 4-bromofluorobenzene. The reference laboratory acceptance criterion for surrogates was 39 to 163 percent recovery.
The method blank matrix is not specified.	The method blank matrix was Ottawa sand. The reference laboratory acceptance criterion for the method blank was less than or equal to the project-specific reporting limit.
The extract duplicate is not specified.	The extract duplicate was analyzed. The reference laboratory acceptance criterion for the extract duplicate was a relative percent difference less than or equal to 25.

Notes:

± = Plus or minus
CCV = Continuing calibration verification
GC = Gas chromatograph
LCS = Laboratory control sample
LCSD = Laboratory control sample duplicate
min = Minute
mL = Milliliter
MS = Matrix spike
MSD = Matrix spike duplicate
ng = Nanogram
SW-846 = "Test Methods for Evaluating Solid Waste"

Table 5-3. Summary of Project-Specific Procedures for EDRO Analysis

SW-846 Method Reference (Step)	Project-Specific Procedures
3540C (Extraction)	
Any free water present in the sample should be decanted and discarded. The sample should then be thoroughly mixed, and any unrepresentative material such as sticks, roots, and stones should be discarded.	During sample homogenization, field sampling technicians attempted to remove unrepresentative material such as sticks, roots, and stones. In addition, the field sampling technicians decanted any free water present in the sample. The reference laboratory did not decant water or remove any unrepresentative material from the sample. The reference laboratory mixed the sample with a stainless-steel tongue depressor.
Ten grams of soil sample should be blended with 10 grams of anhydrous sodium sulfate.	Thirty grams of sample was blended with at least 30 grams of anhydrous sodium sulfate. For medium- and high-level samples, 6 and 2 grams of soil were used for extraction, respectively, and proportionate amounts of anhydrous sodium sulfate were added. The amount of anhydrous sodium sulfate used was not measured gravimetrically but was sufficient to ensure that free moisture was effectively removed from the sample.
Extraction should be performed using 300 mL of extraction solvent.	Extraction was performed using 200 mL of extraction solvent.
Acetone and hexane (1:1 volume per volume) or methylene chloride and acetone (1:1 volume per volume) may be used as the extraction solvent. Note: Methylene chloride and acetone are not constant-boiling solvents and thus are not suitable for the method. Methylene chloride was used as an extraction solvent for method validation.	Methylene chloride was used as the extraction solvent.
The micro Snyder column technique or nitrogen blowdown technique may be used to adjust (concentrate) the soil extract to the required final volume.	Kuderna Danish and nitrogen evaporation were used as the concentration techniques.
Procedures for addressing contamination carryover are not specified.	According to the reference laboratory, a sample extract concentration of 100,000 micrograms per mL is the minimum concentration of EDRO that could result in carryover. Therefore, if a sample extract had a concentration that exceeded the minimum concentration for carryover, the next sample in the sequence was evaluated as follows: (1) if the sample was clean (had no chromatographic peaks), no carryover occurred; (2) if the sample had detectable analyte concentrations (chromatographic peaks), it was reanalyzed under conditions in which carryover did not occur.
8015B (Analysis)	
GC Conditions	
The following GC conditions are recommended: Column: 30-meter x 0.53-millimeter-inside diameter, fused-silica capillary column chemically bonded with 5 percent methyl silicone, 1.5-micrometer field thickness Carrier gas: helium Carrier gas flow rate: 5 to 7 mL/min Makeup gas: helium Makeup gas flow rate: 30 mL/min Injector temperature: 200 °C Detector temperature: 340 °C Temperature program: Initial temperature: 45 °C Hold time: 3 min Program rate: 45 to 275 °C at 12 °C/min Hold time: 12 min Overall time: 34.2 min	An HP 6890 GC was used with the following conditions: Column: 30-meter x 0.53-millimeter-inside diameter, fused-silica capillary column chemically bonded with 5 percent methyl silicone, 1.5-micrometer field thickness Carrier gas: hydrogen Carrier gas flow rate: 1.9 mL/min Makeup gas: hydrogen Makeup gas flow rate: 23 mL/min Injector temperature: 250 °C Detector temperature: 345 °C Temperature program: Initial temperature: 40 °C Hold time: 2 min Program rate: 40 to 345 °C at 30 °C/min Hold time: 5 min Overall time: 17.2 min

Table 5-3. Summary of Project-Specific Procedures for EDRO Analysis (Continued)

SW-846 Method Reference (Step)	Project-Specific Procedures
8015B (Analysis) (Continued)	
Calibration	
The chromatographic system may be calibrated using either internal or external standards.	The chromatographic system was calibrated using external standards with a concentration range equivalent to 75 to 7,500 ng on-column. The reference laboratory acceptance criterion for initial calibration was a relative standard deviation less than or equal to 20 percent of the average response factor or a correlation coefficient for the least-squares linear regression greater than or equal to 0.990.
Calibration should be performed using samples of the specific fuel type contaminating the site. When such samples are not available, recently purchased, commercially available fuel should be used.	Calibration was performed using a commercially available standard that contained even-numbered alkanes from C_{10} through C_{40}.
ICV is not required.	ICV was performed using a second-source standard that contained even-numbered alkanes from C_{10} through C_{40} at a concentration equivalent to 3,750 ng on-column. The reference laboratory acceptance criterion for ICV was an instrument response within 25 percent of the response obtained during initial calibration.
CCV should be performed at the beginning of every 12-hour work shift and at the end of an analytical sequence. CCV throughout the 12-hour shift is also recommended; however, the frequency is not specified.	CCV was performed at the beginning of each analytical batch, after every tenth analysis, and at the end of the analytical batch. The reference laboratory acceptance criteria for CCV were instrument responses within 25 percent (for the closing CCV) and 15 percent (for all other CCVs) of the response obtained during initial calibration.
CCV should be performed using a fuel standard.	CCV was performed using a standard that contained only even-numbered alkanes from C_{10} through C_{40}.
According to SW-846 Method 8000, CCV should be performed at the same concentration as the midpoint concentration of the initial calibration curve; however, the concentration of each calibration point is not specified.	CCV was performed at a concentration equivalent to 3,750 ng on-column.
A method sensitivity check is not required.	A method sensitivity check was performed daily using a calibration standard with a concentration equivalent to 75 ng on-column. The reference laboratory acceptance criterion for the method sensitivity check was detection of the standard.
Retention Time Windows	
The retention time range (window) should be established using C_{10} and C_{28} alkanes during initial calibration. Three measurements should be made over a 72-hour period; the results should be used to determine the average retention time. As a minimum requirement, the retention time should be verified using a midlevel calibration standard at the beginning of each 12-hour shift. Additional analysis of the standard throughout the 12-hour shift is strongly recommended.	Two retention time ranges were established using the opening CCV for each analytical batch. The first range, which was labeled diesel range organics, was marked by the end of the 1,2,4-trimethylbenzene or n-C_{10} peak, whichever occurred later, through the n-octacosane peak. The second range, which was labeled oil range organics, was marked by the end of the n-octacosane peak through the tetracontane peak.
Quantitation	
Quantitation is performed by summing the areas of all chromatographic peaks eluting between n-C_{10} and n-octacosane.	Quantitation was performed by summing the areas of all chromatographic peaks from the end of the 1,2,4-trimethylbenzene or n-C_{10} peak, whichever occurred later, through the n-octacosane peak. A separate quantitation was also performed to sum the areas of all chromatographic peaks from the end of the n-octacosane peak through the tetracontane peak. Separate average response factors for the carbon ranges were used for quantitation. The quantitation results were then summed to determine the total EDRO concentration. All calibrations, ICVs, CCVs, and associated batch quality control measures were controlled for the entire EDRO range using a single quantitation performed over the entire EDRO range.

Table 5-3. Summary of Project-Specific Procedures for EDRO Analysis (Continued)

SW-846 Method Reference (Step)	Project-Specific Procedures
8015B (Analysis) (Continued)	
Quantitation (Continued)	
Subtraction of the baseline rise for the method blank resulting from column bleed is appropriate.	The reference laboratory identified occurrences of baseline rise in the data package. The baseline rise was evaluated during data validation and subtracted when appropriate based on analyst discretion.
Because phthalate esters contaminate many types of products commonly found in the laboratory, consistent quality control should be practiced.	Phthalate peaks were not noted during analysis.
Quality Control	
Spiking compounds for MS/MSDs and LCSs are not specified.	The spiking compound for MS/MSDs and LCSs was an EDRO standard that contained even-numbered alkanes from C_{10} through C_{40}.
According to SW-846 Method 8000, spiking levels for MS/MSDs are determined differently for compliance and noncompliance monitoring applications. For noncompliance applications, the laboratory may spike the sample (1) at the same concentration as the reference sample (LCS), (2) at 20 times the estimated quantitation limit for the matrix of interest, or (3) at a concentration near the middle of the calibration range.	MS/MSD spiking levels were targeted to be between 50 and 150 percent of the unspiked sample concentration. The reference laboratory used historical information to adjust spike amounts or to adjust sample amounts to a preset spike amount. The spiked samples and unspiked samples were prepared such that the sample mass and extract volume used for analysis were the same.
According to SW-846 Method 8000, in-house laboratory acceptance criteria for MS/MSDs and LCSs should be established. As a general rule, the recoveries of most compounds spiked into a sample should fall within the range of 70 to 130 percent, and this range should be used as a guide in evaluating in-house performance.	The reference laboratory acceptance criteria for MS/MSDs and LCSs were a relative percent difference less than or equal to 45 with 46 to 124 percent recovery. The acceptance criteria were based on laboratory historical information. These acceptance criteria are similar to those of the methods cited in Figure 5-1.
The LCS should consist of an aliquot of a clean (control) matrix that is similar to the sample matrix.	The LCS/LCSD matrix was Ottawa sand.
No LCSD is required.	The spiking compound for LCSDs was the EDRO standard that contained even-numbered alkanes from C_{10} through C_{40}.
The surrogate compound and spiking concentration are not specified. According to SW-846 Method 8000, in-house laboratory acceptance criteria for surrogate recoveries should be established.	The surrogate compound was o-terphenyl. The reference laboratory acceptance criterion for surrogates was 45 to 143 percent recovery.
The method blank matrix is not specified.	The method blank matrix was Ottawa sand. The reference laboratory acceptance criterion for the method blank was less than or equal to the project-specific reporting limit.
The extract duplicate is not specified.	The extract duplicate was analyzed. The reference laboratory acceptance criterion for the extract duplicate was a relative percent difference less than or equal to 45.

Notes:

CCV = Continuing calibration verification
GC = Gas chromatograph
ICV = Initial calibration verification
LCS = Laboratory control sample
LCSD = Laboratory control sample duplicate
min = Minute
mL = Milliliter
MS = Matrix spike
MSD = Matrix spike duplicate
n-C_x = Alkane with "x" carbon atoms
ng = Nanogram
SW-846 = "Test Methods for Evaluating Solid Waste"

(1) if a method used offered choices (for example, SW-846 Method 5035 for GRO extraction states that samples may be collected with or without use of a preservative solution), (2) if a method used did not provide specific details (for example, SW-846 Method 5035 for GRO extraction does not specify how unrepresentative material should be handled during sample preparation), or (3) if a modification to a method used was required in order to meet demonstration objectives (for example, SW-846 Method 8015B for EDRO analysis states that quantitation is performed by summing the areas of all chromatographic peaks eluting between the end of the 1,2,4-trimethylbenzene or n-C_{10} peak, whichever occurs later, and the n-octacosane peak; however, an additional quantitation was performed to sum the areas of all chromatographic peaks eluting from the end of the n-octacosane peak through the tetracontane peak in order to meet demonstration objectives).

Before analyzing a liquid PE sample, STL Tampa East added an aliquot of the liquid PE sample to the extraction solvent used for soil samples. A specified aliquot of the liquid PE sample was diluted in methanol for GRO analysis and in methylene chloride for EDRO analysis such that the final volume of the solution for GRO and EDRO analyses was 5.0 and 1.0 mL, respectively. The solution was then analyzed for GRO and EDRO using the same procedures as are used for soil sample extracts.

Chapter 6
Assessment of Reference Method Data Quality

This chapter assesses reference method data quality based on QC check results and PE sample results. A summary of reference method data quality is included at the end of this chapter.

To ensure that the reference method results were of known and adequate quality, EPA representatives performed a predemonstration audit and an in-process audit of the reference laboratory. The predemonstration audit findings were used in developing the predemonstration design. The in-process audit was performed when the laboratory had analyzed a sufficient number of demonstration samples for both GRO and EDRO and had prepared its first data package. During the audit, EPA representatives (1) verified that the laboratory had properly implemented the EPA-approved demonstration plan and (2) performed a critical review of the first data package. All issues identified during the audit were fully addressed by the laboratory before it submitted the subsequent data packages to the EPA. The laboratory also addressed issues identified during the EPA final review of the data packages. Audit findings are summarized in the DER for the demonstration.

6.1 Quality Control Check Results

This section summarizes QC check results for GRO and EDRO analyses performed using the reference method. The QC checks associated with soil sample analyses for GRO and EDRO included method blanks, surrogates, matrix spikes and matrix spike duplicates (MS/MSD), and laboratory control samples and laboratory control sample duplicates (LCS/LCSD). In addition, extract duplicates were analyzed for soil environmental samples. The QC checks associated with liquid PE sample analysis for GRO included method blanks, surrogates, MS/MSDs, and LCS/LCSDs. Because liquid PE sample analyses for EDRO did not include a preparation step, surrogates, MS/MSDs, and LCS/LCSDs were not analyzed; however, an instrument blank was analyzed as a method blank equivalent. The results for the QC checks were compared to project-specific acceptance criteria. These criteria were based on the reference laboratory's historical QC limits and its experience in analyzing the predemonstration investigation samples using the reference method. The reference laboratory's QC limits were established as described in SW-846 and were within the general acceptance criteria recommended by SW-846 for organic analytical methods.

Laboratory duplicates were also analyzed to evaluate the precision associated with percent moisture analysis of soil samples. The acceptance criterion for the laboratory duplicate results was an RPD less than or equal to 20. All laboratory duplicate results met this criterion. The results for the laboratory duplicates are not separately discussed in this ITVR because soil sample TPH results were compared on a wet weight basis except for those used to address primary object P4 (effect of soil moisture content).

6.1.1 GRO Analysis

This section summarizes the results for QC checks used by the reference laboratory during GRO analysis, including method blanks, surrogates, MS/MSDs, extract duplicates, and LCS/LCSDs. A summary of the QC check results is presented at the end of the section.

Method Blanks

Method blanks were analyzed to verify that steps in the analytical procedure did not introduce contaminants that affected analytical results. Ottawa sand and deionized water were used as method blanks for soil and liquid

samples, respectively. These blanks underwent all the procedures required for sample preparation. The results for all method blanks met the acceptance criterion of being less than or equal to the required project-specific reporting limit (5 mg/kg). Based on method blank results, the GRO analysis results were considered to be valid.

Surrogates

Each soil investigative and QC sample for GRO analysis was spiked with a surrogate, 4-bromofluorobenzene, before extraction to determine whether significant matrix effects existed within the sample and to estimate the efficiency of analyte recovery during sample preparation and analysis. A diluted, liquid PE sample was also spiked with the surrogate during sample preparation. The initial surrogate spiking levels for soil and liquid PE samples were 2 mg/kg and 40 microgram per liter (µg/L), respectively. The acceptance criterion was 39 to 163 percent surrogate recovery. For samples analyzed at a dilution factor greater than four, the surrogate concentration was diluted to a level below the reference laboratory's reporting limit for the reference method; therefore, surrogate recoveries for these samples were not used to assess impacts on data quality.

A total of 101 surrogate measurements were made during analysis of environmental and associated QC samples. Fifty-six of these samples were analyzed at a dilution factor less than or equal to four. The surrogate recoveries for these 56 samples ranged from 43 to 345 percent with a mean recovery of 150 percent and a median recovery of 136 percent. Because the mean and median recoveries were greater than 100 percent, an overall positive bias was indicated.

The surrogate recoveries for 16 of the 56 samples did not meet the acceptance criterion. In each case, the surrogate was recovered at a concentration above the upper limit of the acceptance criterion. Examination of the gas chromatograms for the 16 samples revealed that some PHCs or naturally occurring interferents present in these environmental samples coeluted with the surrogate, resulting in higher surrogate recoveries. Such coelution is typical for hydrocarbon-containing samples analyzed using a GC/FID technique, which was the technique used in the reference method. The surrogate recoveries for QC samples such as method blanks and LCS/LCSDs met the acceptance criterion, indicating that the laboratory sample preparation and analysis procedures were in control. Because the coelution was observed only for environmental samples and because the surrogate recoveries for QC samples met the acceptance criterion, the reference laboratory did not reanalyze the environmental samples with high surrogate recoveries. Calculations performed to evaluate whether the coelution resulted in underreporting of GRO concentrations indicated an insignificant impact of less than 3 percent. Based on the surrogate results for environmental and associated QC samples, the GRO analysis results for environmental samples were considered to be valid.

A total of 42 surrogate measurements were made during the analysis of soil PE and associated QC samples. Thirty-four of these samples were analyzed at a dilution factor less than or equal to four. The surrogate recoveries for these 34 samples ranged from 87 to 108 percent with a mean recovery of 96 percent and a median recovery of 95 percent. The surrogate recoveries for all 34 samples met the acceptance criterion. Based on the surrogate results for soil PE and associated QC samples, the GRO analysis results for soil PE samples were considered to be valid.

A total of 37 surrogate measurements were made during the analysis of liquid PE and associated QC samples. Six of these samples were analyzed at a dilution factor less than or equal to four. All six samples were QC samples (method blanks and LCS/LCSDs). The surrogate recoveries for these six samples ranged from 81 to 84 percent, indicating a small negative bias. However, the surrogate recoveries for all six samples met the acceptance criterion. Based on the surrogate results for liquid PE and associated QC samples, the GRO analysis results for liquid PE samples were considered to be valid.

Matrix Spikes and Matrix Spike Duplicates

MS/MSD results were evaluated to determine the accuracy and precision of the analytical results with respect to the effects of the sample matrix. For GRO analysis, each soil sample designated as an MS or MSD was spiked with the GRO calibration standard at an initial spiking level of 20 mg/kg. MS/MSDs were also prepared for liquid PE samples. Each diluted, liquid PE sample designated as an MS or MSD was spiked with the GRO calibration standard at an initial spiking level of 40 µg/L. The acceptance criteria for MS/MSDs were 33 to 115 percent recovery and an RPD less than or equal to 25. When the MS/MSD percent recovery acceptance criterion was not met, instead

of attributing the failure to meet the criterion to an inappropriate spiking level, the reference laboratory respiked the sample at a more appropriate and practical spiking level. Information on the selection of the spiking level and calculation of percent recoveries for MS/MSD samples is provided below.

According to Provost and Elder (1983), for percent recovery data to be reliable, spiking levels should be at least five times the unspiked sample concentration. For the demonstration, however, a large number of the unspiked sample concentrations were expected to range between 1,000 and 10,000 mg/kg, so use of such high spiking levels was not practical. Therefore, a target spiking level of 50 to 150 percent of the unspiked sample concentration was used for the demonstration. Provost and Elder (1983) also present an alternate approach for calculating percent recoveries for MS/MSD samples (100 times the ratio of the measured concentration in a spiked sample to the calculated concentration in the sample). However, for the demonstration, percent recoveries were calculated using the traditional approach (100 times the ratio of the amount recovered to the amount spiked) primarily because the alternate approach is not commonly used.

For environmental samples, a total of 10 MS/MSD pairs were analyzed. Four sample pairs collected in the NEX Service Station Area were designated as MS/MSDs. The sample matrix in this area primarily consisted of medium-grained sand. The percent recoveries for all but one of the MS/MSD samples ranged from 67 to 115 with RPDs ranging from 2 to 14. Only one MS sample with a 162 percent recovery did not meet the percent recovery acceptance criterion; however, the RPD acceptance criterion for the MS/MSD and the percent recovery and RPD acceptance criteria for the LCS/LCSD associated with the analytical batch for this sample were met. Based on the MS/MSD results, the GRO analysis results for the NEX Service Station Area samples were considered to be valid.

Two sample pairs collected in the B-38 Area were designated as MS/MSDs. The sample matrix in this area primarily consisted of sand and clay. The percent recoveries for the MS/MSD samples ranged from 60 to 94 with RPDs of 1 and 13. Therefore, the percent recoveries and RPDs for these samples met the acceptance criteria. Based on the MS/MSD results, the GRO analysis results for the B-38 Area samples were considered to be valid.

Four sample pairs collected in the SFT Area were designated as MS/MSDs. The sample matrix in this area primarily consisted of silty clay. The percent recoveries for the MS/MSD samples ranged from 0 to 127 with RPDs ranging from 4 to 21. Of the four sample pairs, two sample pairs met the percent recovery acceptance criterion, one sample pair exhibited percent recoveries less than the lower acceptance limit, and one sample pair exhibited percent recoveries greater than the upper acceptance limit. For the two sample pairs that did not meet the percent recovery acceptance criterion, the RPD acceptance criterion for the MS/MSDs and the percent recovery and RPD acceptance criteria for the LCS/LCSDs associated with the analytical batches for these samples were met. Because of the varied percent recoveries for the MS/MSD sample pairs, it was not possible to conclude whether the GRO analysis results for the SFT Area samples had a negative or positive bias. Although one-half of the MS/MSD results did not meet the percent recovery acceptance criterion, the out-of-control situations alone did not constitute adequate grounds for rejection of any of the GRO analysis results for the SFT Area samples. The out-of-control situations may have been associated with inadequate spiking levels (0.7 to 2.8 times the unspiked sample concentrations compared to the minimum recommended value of 5 times the concentrations).

Three soil PE sample pairs were designated as MS/MSDs. The sample matrix for these samples consisted of silty sand. The percent recoveries for these samples ranged from 88 to 103 with RPDs ranging from 4 to 6. The percent recoveries and RPDs for these samples met the acceptance criteria. Based on the MS/MSD results, the GRO analysis results for the soil PE samples were considered to be valid.

Two liquid PE sample pairs were designated as MS/MSDs. The percent recoveries for these samples ranged from 77 to 87 with RPDs of 1 and 5. The percent recoveries and RPDs for these samples met the acceptance criteria. Based on the MS/MSD results, the GRO analysis results for the liquid PE samples were considered to be valid.

Extract Duplicates

For GRO analysis, after soil sample extraction, extract duplicates were analyzed to evaluate the precision associated with the reference laboratory's analytical procedure. The reference laboratory sampled duplicate

aliquots of the GRO extracts for analysis. The acceptance criterion for extract duplicate precision was an RPD less than or equal to 25. Two or more environmental samples collected in each demonstration area whose samples were analyzed for GRO (the NEX Service Station, B-38, and SFT Areas) were designated as extract duplicates. A total of 10 samples designated as extract duplicates were analyzed for GRO. The RPDs for these samples ranged from 0.5 to 11. Therefore, the RPDs for all the extract duplicates met the acceptance criterion. Based on the extract duplicate results, the GRO analysis results were considered to be valid.

Laboratory Control Samples and Laboratory Control Sample Duplicates

For GRO analysis, LCS/LCSD results were evaluated to determine the accuracy and precision associated with control samples prepared by the reference laboratory. To generate a soil LCS or LCSD, Ottawa sand was spiked with the GRO calibration standard at a spiking level of 20 mg/kg. To generate an LCS or LCSD for liquid PE sample analysis, deionized water was spiked with the GRO calibration standard at a spiking level of 40 µg/L. The acceptance criteria for LCS/LCSDs were 33 to 115 percent recovery and an RPD less than or equal to 25. The LCS/LCSD acceptance criteria were based on the reference laboratory's historical data.

Ten pairs of soil LCS/LCSD samples were prepared and analyzed. The percent recoveries for these samples ranged from 87 to 110 with RPDs ranging from 2 to 14. In addition, two pairs of liquid LCS/LCSD samples were prepared and analyzed. The percent recoveries for these samples ranged from 91 to 92 with RPDs equal to 0 and 1. Therefore, the percent recoveries and RPDs for the soil and liquid LCS/LCSD samples met the acceptance criteria, indicating that the GRO analysis procedure was in control. Based on the LCS/LCSD results, the GRO analysis results were considered to be valid.

Summary of Quality Control Check Results

Table 6-1 summarizes the QC check results for GRO analysis. Based on the QC check results, the conclusions presented below were drawn regarding the accuracy and precision of GRO analysis results for the demonstration.

The project-specific percent recovery acceptance criteria were met for most environmental samples and all PE samples. As expected, the percent recovery ranges were broader for the environmental samples than for the PE samples. As indicated by the mean and median percent recoveries, the QC check results generally indicated a slight negative bias (up to 20 percent) in the GRO concentration measurements; the exceptions were the surrogate recoveries for environmental samples and the LCS/LCSD recoveries for soil PE samples. The observed bias did not exceed the generally acceptable bias (±30 percent) stated in SW-846 for organic analyses and is typical for most organic analytical methods for environmental samples. Because the percent recovery ranges were sometimes above and sometimes below 100, the observed bias did not appear to be systematic.

The project-specific RPD acceptance criterion was met for all samples. As expected, the RPD range and the mean and median RPDs for MS/MSDs associated with the soil environmental samples were greater than those for other QC checks and matrixes listed in Table 6-1. The low RPDs observed indicated good precision in the GRO concentration measurements made during the demonstration.

6.1.2 EDRO Analysis

This section summarizes the results for QC checks used by the reference laboratory during EDRO analysis, including method and instrument blanks, surrogates, MS/MSDs, extract duplicates, and LCS/LCSDs. A summary of the QC check results is presented at the end of the section.

Method and Instrument Blanks

Method and instrument blanks were analyzed to verify that steps in the analytical procedures did not introduce contaminants that affected analytical results. Ottawa sand was used as a method blank for soil samples. The method blanks underwent all the procedures required for sample preparation. For liquid PE samples, the extraction solvent (methylene chloride) was used as an instrument blank. The results for all method and instrument blanks met the acceptance criterion of being less than or equal to the required project-specific reporting limit (10 mg/kg). Based on the method and instrument blank results, the EDRO analysis results were considered to be valid.

Table 6-1. Summary of Quality Control Check Results for GRO Analysis

QC Check[a]	Matrix Associated with QC Check	No. of Measurements Used to Evaluate Data Quality	Accuracy (Percent Recovery)					Precision (Relative Percent Difference)				
			Acceptance Criterion	Actual Range	No. of Measurements Meeting Acceptance Criterion	Mean	Median	Acceptance Criterion	Actual Range	No. of Measurements Meeting Acceptance Criterion	Mean	Median
Surrogate	Soil environmental samples	56	39 to 163	43 to 345	40	150	136	Not applicable				
	Soil PE samples	34		87 to 108	34	96	95					
	Liquid PE samples	6		81 to 84	6	83	84					
MS/MSD	Soil environmental samples	20 (10 pairs)	33 to 115	0 to 162	15	81	80	≤25	1 to 21	10 pairs	11	12
	Soil PE samples	6 (3 pairs)		88 to 103	6	94	92		4 to 6	3 pairs	5	5
	Liquid PE samples	4 (2 pairs)		77 to 87	4	83	85		1 to 5	2 pairs	3	3
Extract duplicate	Soil environmental samples	10 pairs	Not applicable						0.5 to 11	10 pairs	5	4
LCS/LCSD	Soil environmental and PE samples	10 pairs	33 to 115	87 to 110	20	100	100		2 to 14	10 pairs	6	6
	Liquid PE samples	2 pairs		91 to 92	4	92	92		0 to 1	2 pairs	0.5	0.5

Notes:

≤ = Less than or equal to
LCS/LCSD = Laboratory control sample and laboratory control sample duplicate
MS/MSD = Matrix spike and matrix spike duplicate
PE = Performance evaluation
QC = Quality control

[a] During the demonstration, 12 method blanks (10 for soil samples and 2 for liquid samples) were analyzed. The method blank results met the project-specific acceptance criteria.

Surrogates

Each soil investigative and QC sample for EDRO analysis was spiked with a surrogate, o-terphenyl, before extraction to determine whether significant matrix effects existed within the sample and to estimate the efficiency of analyte recovery during sample preparation and analysis. For a 30-gram sample, the spike concentration was 3.3 mg/kg. For samples with higher EDRO concentrations, for which smaller sample amounts were used during extraction, the spiking levels were proportionately higher. The acceptance criterion was 45 to 143 percent surrogate recovery. Liquid PE samples for EDRO analysis were not spiked with a surrogate because the analysis did not include a sample preparation step.

A total of 185 surrogate measurements were made during analysis of environmental and associated QC samples. Six of these samples did not meet the percent recovery acceptance criterion. Four of the six samples were environmental samples. When the reference laboratory reanalyzed the four samples, the surrogate recoveries for the samples met the acceptance criterion; therefore, the reference laboratory reported the EDRO concentrations measured during the reanalyses. The remaining two samples for which the surrogate recoveries did not meet the acceptance criterion were LCS/LCSD samples; these samples had low surrogate recoveries. According to the reference laboratory, these low recoveries were due to the extracts going dry during the extract concentration procedure. Because two samples were laboratory QC samples, the reference laboratory reanalyzed them as well as all the other samples in the QC lot; during the reanalyses, all surrogate recoveries met the acceptance criterion. The surrogate recoveries for all results reported ranged from 45 to 143 percent with mean and median recoveries of 77 percent, indicating an overall negative bias. The surrogate recoveries for all reported sample results met the acceptance criterion. Based on the surrogate results for environmental and associated QC samples, the EDRO analysis results were considered to be valid.

A total of 190 surrogate measurements were made during analysis of soil PE and associated QC samples. Five of these samples did not meet the percent recovery acceptance criterion. In each case, the surrogate was recovered at a concentration below the lower limit of the acceptance criterion. Three of the five samples were soil PE samples, and the remaining two samples were LCS/LCSDs. The reference laboratory reanalyzed the three soil PE samples and the LCS/LCSD pair as well as all the other samples in the QC lot associated with the LCS/LCSDs; during the reanalyses, all surrogate recoveries met the acceptance criterion. The surrogate recoveries for all results reported ranged from 46 to 143 percent with mean and median recoveries of 76 percent, indicating an overall negative bias. The surrogate recoveries for all reported sample results met the acceptance criterion. Based on the surrogate results for soil PE and associated QC samples, the EDRO analysis results were considered to be valid.

Matrix Spikes and Matrix Spike Duplicates

MS/MSD results were evaluated to determine the accuracy and precision of the analytical results with respect to the effects of the sample matrix. For EDRO analysis, each soil sample designated as an MS or MSD was spiked with the EDRO calibration standard at an initial spiking level of 50 mg/kg when a 30-gram sample was used during extraction. The initial spiking levels were proportionately higher when smaller sample amounts were used during extraction. The acceptance criteria for MS/MSDs were 46 to 124 percent recovery and an RPD less than or equal to 45. When the MS/MSD percent recovery acceptance criterion was not met, instead of attributing the failure to meet the criterion to an inappropriate spiking level, the reference laboratory respiked the samples at a target spiking level between 50 and 150 percent of the unspiked sample concentration. Additional information on spiking level selection for MS/MSDs is presented in Section 6.1.1. No MS/MSDs were prepared for liquid PE samples for EDRO analysis because the analysis did not include a sample preparation step.

For environmental samples, a total of 13 MS/MSD pairs were analyzed. Two sample pairs collected in the FFA were designated as MS/MSDs. The sample matrix in this area primarily consisted of medium-grained sand. The percent recoveries for the MS/MSD samples ranged from 0 to 183 with RPDs of 0 and 19. One of the two sample pairs exhibited percent recoveries less than the lower acceptance limit. In the second sample pair, one sample exhibited a percent recovery less than the lower acceptance limit, and one sample exhibited a percent recovery greater than the upper acceptance limit. For both sample pairs, the RPD acceptance criterion for the MS/MSDs and the percent recovery and RPD acceptance criteria for the LCS/LCSDs associated with the analytical

batches for these samples were met. Because of the varied percent recoveries for the MS/MSD sample pairs, it was not possible to conclude whether the EDRO analysis results for the FFA samples had a negative or positive bias. Although the MS/MSD results did not meet the percent recovery acceptance criterion, the out-of-control situations alone did not constitute adequate grounds for rejection of any of the EDRO analysis results for the FFA samples. The out-of-control situations may have been associated with inadequate spiking levels (0.1 to 0.5 times the unspiked sample concentrations compared to the minimum recommended value of 5 times the concentrations).

Four sample pairs collected in the NEX Service Station Area were designated as MS/MSDs. The sample matrix in this area primarily consisted of medium-grained sand. The percent recoveries for the MS/MSD samples ranged from 81 to 109 with RPDs ranging from 4 to 20. The percent recoveries and RPDs for these samples met the acceptance criteria. Based on the MS/MSD results, the EDRO analysis results for the NEX Service Station Area samples were considered to be valid.

One sample pair collected in the PRA was designated as an MS/MSD. The sample matrix in this area primarily consisted of silty sand. The percent recoveries for the MS/MSD samples were 20 and 80 with an RPD equal to 19. One sample exhibited a percent recovery less than the lower acceptance limit, whereas the percent recovery for the other sample met the acceptance criterion. The RPD acceptance criterion for the MS/MSD and the percent recovery and RPD acceptance criteria for the LCS/LCSD associated with the analytical batch for this sample pair were met. Although the percent recoveries for the MS/MSD sample pair may indicate a negative bias, because the MS/MSD results for only one sample pair were available, it was not possible to conclude that the EDRO analysis results for the PRA samples had a negative bias. Although one of the percent recoveries for the MS/MSD did not meet the acceptance criterion, the out-of-control situation alone did not constitute adequate grounds for rejection of any of the EDRO analysis results for the PRA samples. The out-of-control situation may have been associated with inadequate spiking levels (0.4 times the unspiked sample concentration compared to the minimum recommended value of 5 times the concentration).

Two sample pairs collected in the B-38 Area were designated as MS/MSDs. The sample matrix in this area primarily consisted of sand and clay. The percent recoveries for the MS/MSD samples ranged from 25 to 77 with RPDs of 6 and 11. Of the two sample pairs, one sample pair met the percent recovery acceptance criterion, and one sample pair exhibited percent recoveries less than the lower acceptance limit. For the sample pair that did not meet the percent recovery acceptance criterion, the RPD acceptance criterion for the MS/MSDs and the percent recovery and RPD acceptance criteria for the LCS/LCSDs associated with the analytical batch for the sample pair were met. Although the percent recoveries for one MS/MSD sample pair indicated a negative bias, because the percent recoveries for the other sample pair were acceptable, it was not possible to conclude that the EDRO analysis results for the B-38 Area samples had a negative bias. Although one-half of the MS/MSD results did not meet the percent recovery acceptance criterion, the out-of-control situations alone did not constitute adequate grounds for rejection of any of the EDRO analysis results for the B-38 Area samples. The out-of-control situations may have been associated with inadequate spiking levels (1.4 times the unspiked sample concentrations compared to the minimum recommended value of 5 times the concentrations).

Four sample pairs collected in the SFT Area were designated as MS/MSDs. The sample matrix in this area primarily consisted of silty clay. The percent recoveries for the MS/MSD samples ranged from 0 to 223 with RPDs ranging from 8 to 50. Of the four sample pairs, three sample pairs had one sample each that exhibited a percent recovery less than the lower acceptance limit and one sample pair had one sample that exhibited a percent recovery greater than the upper acceptance limit. The RPD acceptance criterion was met for all but one of the MS/MSDs. The percent recovery and RPD acceptance criteria for the LCS/LCSDs associated with the analytical batches for these samples were met. Because of the varied percent recoveries for the MS/MSD sample pairs, it was not possible to conclude whether the EDRO analysis results for the SFT Area samples had a negative or positive bias. Although one-half of the MS/MSD results did not meet the percent recovery acceptance criterion and one of the four sample pairs did not meet the RPD acceptance criterion, the out-of-control situations alone did not constitute adequate grounds for rejection of any of the EDRO analysis results for the SFT Area samples. The out-of-control situations may have been associated with inadequate spiking levels (0.4 to 0.7 times the unspiked

sample concentrations compared to the minimum recommended value of 5 times the concentrations).

Five soil PE sample pairs were designated as MS/MSDs. The sample matrix for these samples primarily consisted of silty sand. The percent recoveries for these samples ranged from 0 to 146 with RPDs ranging from 3 to 17. Of the five sample pairs, three sample pairs met the percent recovery acceptance criterion, one sample pair exhibited percent recoveries less than the lower acceptance limit, and one sample pair exhibited percent recoveries greater than the upper acceptance limit. For the two sample pairs that did not meet the percent recovery acceptance criterion, the RPD acceptance criterion for the MS/MSDs and the percent recovery and RPD acceptance criteria for the LCS/LCSDs associated with the analytical batches for these samples were met. Because of the varied percent recoveries for the MS/MSD sample pairs, it was not possible to conclude whether the EDRO analysis results for the soil PE samples had a negative or positive bias. Although the percent recoveries for two of the five sample MS/MSD pairs did not meet the acceptance criterion, the out-of-control situations alone did not constitute adequate grounds for rejection of any of the EDRO analysis results for the soil PE samples.

Extract Duplicates

For EDRO analysis, after soil sample extraction, extract duplicates were analyzed to evaluate the precision associated with the reference laboratory's analytical procedure. The reference laboratory sampled duplicate aliquots of the EDRO extracts for analysis. The acceptance criterion for extract duplicate precision was an RPD less than or equal to 45. One or more environmental samples collected in each demonstration area were designated as extract duplicates. A total of 13 samples designated as extract duplicates were analyzed for EDRO. The RPDs for these samples ranged from 0 to 11 except for one extract duplicate pair collected in the SFT Area that had an RPD equal to 34. The RPDs for all the extract duplicates met the acceptance criterion. Based on the extract duplicate results, all EDRO results were considered to be valid.

Laboratory Control Samples and Laboratory Control Sample Duplicates

For EDRO analysis, LCS/LCSD results were evaluated to determine the accuracy and precision associated with control samples prepared by the reference laboratory. To generate a soil LCS or LCSD, Ottawa sand was spiked with the EDRO calibration standard at a spiking level of 50 mg/kg. The acceptance criteria for LCS/LCSDs were 46 to 124 percent recovery and an RPD less than or equal to 45. The LCS/LCSD acceptance criteria were based on the reference laboratory's historical data. No LCS/LCSDs were prepared for liquid PE samples for EDRO analysis because the analysis did not include a sample preparation step.

Twenty-two pairs of LCS/LCSD samples were prepared and analyzed. The percent recoveries for these samples ranged from 47 to 88 with RPDs ranging from 0 to 29. Therefore, the percent recoveries and RPDs for these samples met the acceptance criteria, indicating that the EDRO analysis procedure was in control. Based on the LCS/LCSD results, the EDRO analysis results were considered to be valid.

Summary of Quality Control Check Results

Table 6-2 summarizes the QC check results for EDRO analysis. Based on the QC check results, the conclusions presented below were drawn regarding the accuracy and precision of EDRO analysis results for the demonstration.

The project-specific percent recovery acceptance criteria were met for all surrogates and LCS/LCSDs. About one-half of the MS/MSDs did not meet the percent recovery acceptance criterion. As expected, the MS/MSD percent recovery range was broader for environmental samples than for PE samples. The mean and median percent recoveries for all the QC check samples indicated a negative bias (up to 33 percent) in the EDRO concentration measurements. Although the observed bias was slightly greater than the generally acceptable bias (±30 percent) stated in SW-846 for organic analyses, the observed recoveries were not atypical for most organic analytical methods for environmental samples. Because the percent recovery ranges were sometimes above and sometimes below 100, the observed bias did not appear to be systematic.

The project-specific RPD acceptance criterion was met for all samples except one environmental MS/MSD sample pair. As expected, the RPD range and the mean and median RPDs for MS/MSDs associated with the soil environmental samples were greater than those for other QC checks and matrixes listed in Table 6-2. The low

Table 6-2. Summary of Quality Control Check Results for EDRO Analysis

QC Check[a]	Matrix Associated with QC Check	No. of Measurements Used to Evaluate Data Quality	Accuracy (Percent Recovery)					Precision (Relative Percent Difference)				
			Acceptance Criterion	Actual Range	No. of Measurements Meeting Acceptance Criterion	Mean	Median	Acceptance Criterion	Actual Range	No. of Measurements Meeting Acceptance Criterion	Mean	Median
Surrogate	Soil environmental samples	179	45 to 143	45 to 143	179	77	77	Not applicable				
	Soil PE samples	185		46 to 143	185	76	76					
MS/MSD	Soil environmental samples	26 (13 pairs)	46 to 124	0 to 223	14	67	79	≤45	0 to 50	12 pairs	17	16
	Soil PE samples	10 (5 pairs)		0 to 146	6	75	78		3 to 17	5 pairs	7	4
Extract duplicate	Soil environmental samples	13 pairs	Not applicable						0 to 34	13 pairs	6	2
LCS/LCSD	Soil environmental and PE samples	44 (22 pairs)	46 to 124	47 to 88	44	77	80		0 to 29	22 pairs	6	5

Notes:

≤ = Less than or equal to
LCS/LCSD = Laboratory control sample and laboratory control sample duplicate
MS/MSD = Matrix spike and matrix spike duplicate
PE = Performance evaluation
QC = Quality control

[a] During the demonstration, 22 method blanks for soil samples and 2 instrument blanks for liquid samples were analyzed. The blank results met the project-specific acceptance criteria.

RPDs observed indicated good precision in the EDRO concentration measurements made during the demonstration.

6.2 Selected Performance Evaluation Sample Results

Soil and liquid PE samples were analyzed during the demonstration to document the reference method's performance in analyzing samples prepared under controlled conditions. The PE sample results coupled with the QC check results were used to establish the reference method's performance in such a way that the overall assessment of the reference method would support interpretation of the PetroFLAG™ System's performance, which is discussed in Chapter 7. Soil PE samples were prepared by adding weathered gasoline or diesel to Ottawa sand or processed garden soil. For each sample, an amount of weathered gasoline or diesel was added to the sample matrix in order to prepare a PE sample with a low (less than 100 mg/kg), medium (100 to 1,000 mg/kg), or high (greater than 1,000 mg/kg) TPH concentration. Liquid PE samples consisted of neat materials. Triplicate samples of each type of PE sample were analyzed by the reference laboratory except for the low-concentration-range PE samples, for which seven replicate samples were analyzed.

As described in Section 4.2, some PE samples also contained interferents. Section 6.2 does not discuss the reference method results for PE samples containing interferents because the results address a specific demonstration objective. To facilitate comparisons, the reference method results that directly address demonstration objectives are discussed along with the PetroFLAG™ System results in Chapter 7. Section 6.2 presents a comparison of the reference method's mean TPH results for selected PE samples to the certified values and performance acceptance limits provided by ERA, a commercial PE sample provider that prepared the PE samples for the demonstration. Although the reference laboratory reported sample results for GRO and EDRO analyses separately, because ERA provided certified values and performance acceptance limits, the reference method's mean TPH results (GRO plus EDRO analysis results) were used for comparison.

For soil samples containing weathered gasoline, the certified values used for comparison to the reference method results were based on mean TPH results for triplicate samples analyzed by ERA using a GC/FID method. ERA extracted the PE samples on the day that PE samples were shipped to the Navy BVC site for distribution to the reference laboratory and developers. The reference laboratory completed methanol extraction of the demonstration samples within 2 days of receiving them. Between 5 and 7 days elapsed between the time that ERA and the time that the reference laboratory completed methanol extractions of the demonstration samples. The difference in extraction times is not believed to have had a significant effect on the reference method's TPH results because the samples for GRO analysis were containerized in EPA-approved EnCores and were stored at 4 ± 2 °C to minimize volatilization. After methanol extraction of the PE samples, both ERA and the reference laboratory analyzed the sample extracts within the appropriate holding times for the extracts.

For soil samples containing diesel, the certified values were established by calculating the TPH concentrations based on the amounts of diesel spiked into known quantities of soil; these samples were not analyzed by ERA. Similarly, the densities of the neat materials were used as the certified values for the liquid PE samples.

The performance acceptance limits for soil PE samples were based on ERA's historical data on percent recoveries and RSDs from multiple laboratories that had analyzed similarly prepared ERA PE samples using a GC method. The performance acceptance limits were determined at the 95 percent confidence level using Equation 6-1.

$$\text{Performance Acceptance Limits} = \text{Certified Value} \times (\text{Average Percent Recovery} \pm 2(\text{Average RSD})) \quad (6\text{-}1)$$

According to SW-846, the 95 percent confidence limits should be treated as warning limits, whereas the 99 percent confidence limits should be treated as control limits. The 99 percent confidence limits are calculated by using three times the average RSD in Equation 6-1 instead of two times the average RSD.

When establishing the performance acceptance limits, ERA did not account for variables among the multiple laboratories, such as different extraction and analytical methods, calibration procedures, and chromatogram integration ranges (beginning and end points). For this reason, the performance acceptance limits should be used with caution.

Performance acceptance limits for liquid PE samples were not available because ERA did not have historical information on percent recoveries and RSDs for the neat materials used in the demonstration.

Table 6-3 presents the PE sample types, TPH concentration ranges, performance acceptance limits, certified values, reference method mean TPH concentrations, and ratios of reference method mean TPH concentrations to certified values.

In addition to the samples listed in Table 6-3, three blank soil PE samples (processed garden soil) were analyzed to determine whether the soil PE sample matrix contained a significant TPH concentration. Reference method GRO results for all triplicate samples were below the reporting limit of 0.54 mg/kg. Reference method EDRO results were calculated by adding the results for DRO and oil range organics (ORO) analyses. For one of the triplicate samples, both the DRO and ORO results were below the reporting limits of 4.61 and 5.10 mg/kg, respectively. For the remaining two triplicates, the DRO and ORO results were 1.5 times greater than the reporting limits. Based on the TPH concentrations in the medium- and high-concentration-range soil PE samples listed in Table 6-3, the contribution of the processed garden soil to the TPH concentrations was insignificant and ranged between 0.5 and 5 percent.

The reference method's mean TPH results for the soil PE samples listed in Table 6-3 were within the performance acceptance limits except for the low-concentration-range diesel samples. For the low-range diesel samples, (1) the individual TPH concentrations for all seven replicates were less than the lower performance acceptance limit and (2) the upper 95 percent confidence limit for TPH results was also less than the lower performance acceptance limit. However, the reference method mean and individual TPH results for the low-range diesel samples were within the 99 percent confidence interval of 10.8 to 54.6 mg/kg, indicating that the reference method results met the control limits but not the warning limits. Collectively, these observations indicated a negative bias in TPH measurements for low-range diesel samples.

Table 6-3. Comparison of Soil and Liquid Performance Evaluation Sample Results

Sample Type[a]	TPH Concentration Range	Performance Acceptance Limits (mg/kg)	Certified Value	Reference Method Mean TPH Concentration	Reference Method Mean TPH Concentration/ Certified Value (percent)
Soil Sample (Ottawa Sand)					
Diesel	Low	18.1 to 47.4	37.3 mg/kg	15.4 mg/kg	41
Soil Samples (Processed Garden Soil)					
Weathered gasoline	Medium	389 to 1,548	1,090 mg/kg	705 mg/kg	65
	High	1,110 to 4,430	3,120 mg/kg	2,030 mg/kg	65
Weathered gasoline at 16 percent moisture	High	992 to 3,950	2,780 mg/kg	1,920 mg/kg	69
Diesel	Medium	220 to 577	454 mg/kg	252 mg/kg	56
	High	1,900 to 4,980	3,920 mg/kg	2,720 mg/kg	69
Diesel at less than 1 percent moisture	High	2,100 to 5,490	4,320 mg/kg	2,910 mg/kg	67
Liquid Samples					
Weathered gasoline	High	Not available	814,100 mg/L	648,000 mg/L	80
Diesel	High	Not available	851,900 mg/L	1,090,000 mg/L	128

Notes:

mg/kg = Milligram per kilogram
mg/L = Milligram per liter

[a] Soil samples were prepared at 9 percent moisture unless stated otherwise.

As noted above, Table 6-3 presents ratios of the reference method mean TPH concentrations to the certified values for PE samples. The ratios for weathered gasoline-containing soil samples ranged from 65 to 69 percent and did not appear to depend on whether the samples were medium- or high-range samples. The ratio for neat, weathered gasoline (liquid sample) was 80 percent, which was 11 to 15 percentage points greater than the ratios for the soil samples. The difference in the ratios may be attributed to (1) potential loss of volatiles during soil sample transport and storage and during soil sample handling when extractions were performed and (2) lower analyte recovery during soil sample extraction. The less than 100 percent ratios observed indicated a negative bias in TPH measurement for soil and liquid samples containing weathered gasoline. The observed bias for the liquid samples did not exceed the generally acceptable bias (±30 percent) stated in SW-846 for most organic analyses. However, the bias for soil samples exceeded the acceptable bias by up to 5 percentage points.

The ratios for diesel-containing soil samples ranged from 41 to 69 percent and increased with increases in the TPH concentration range. The ratio for neat diesel (liquid sample) was 128 percent, which was substantially greater than the ratios for soil samples. Collectively, the negative bias observed for soil samples and the positive bias observed for liquid samples indicated a low analyte recovery during soil sample extraction because the soil and liquid samples were analyzed using the same calibration procedures but only the soil samples required extraction before analysis. The extraction procedure used during the demonstration is an EPA-approved method that is widely used by commercial laboratories in the United States. Details on the extraction procedure are presented in Table 5-3 of this ITVR.

The positive bias observed for liquid samples did not exceed the generally acceptable bias stated in SW-846. The negative bias observed for high-concentration-range soil samples exceeded the acceptable bias by an average of 2 percentage points. However, the negative bias observed for low- and medium-range samples exceeded the acceptable bias by 29 and 14 percentage points, respectively, indicating a negative bias.

Because the reference method results exhibited a negative bias for soil PE samples when compared to ERA-certified values, ERA's historical data on percent recoveries and RSDs from multiple laboratories were examined. Table 6-4 compares ERA's historical percent recoveries and RSDs to the reference method percent recoveries and RSDs obtained during the demonstration. Table 6-4 shows that ERA's historical recoveries also exhibited a negative bias for all sample types except weathered gasoline in water and that the reference method recoveries were less than ERA's historical recoveries for all sample types except diesel in water. The ratios of reference method mean recoveries to ERA historical mean recoveries for weathered gasoline-containing samples indicated that the reference method TPH results were 26 percent less than ERA's historical recoveries. The reference method recoveries for diesel-containing (1) soil samples were 34 percent less than the ERA historical recoveries and (2) water samples were 63 percent greater than the ERA historical recoveries. In all cases, the RSDs for the reference method were significantly lower than ERA's historical RSDs, indicating that the reference method

Table 6-4. Comparison of Environmental Resource Associates Historical Results to Reference Method Results

	ERA Historical Results		Reference Method Results		
Sample Type	Mean Recovery (percent)	Mean Relative Standard Deviation (percent)	Mean Recovery[a] (percent)	Reference Method Mean Recovery/ERA Historical Mean Recovery (percent)	Mean Relative Standard Deviation[a] (percent)
Weathered gasoline in soil	88.7	26.5	66	75	7
Diesel in soil	87.7	19.6	58	66	9
Weathered gasoline in water	109	22.0	80	73	5
Diesel in water	78.5	22.8	128	163	6

Notes:

ERA = Environmental Resource Associates

[a] The reference method mean recovery and mean relative standard deviation were based on recoveries and relative standard deviations observed for all concentration ranges for a given type of performance evaluation sample.

achieved significantly greater precision. The greater precision observed for the reference method during the demonstration may be associated with the fact that the reference method was implemented by a single laboratory, whereas ERA's historical RSDs were based on results obtained from multiple laboratories that may have used different analytical protocols.

In summary, compared to ERA-certified values, the TPH results for all PE sample types except neat diesel exhibited a negative bias to a varying degree; the TPH results for neat diesel exhibited a positive bias of 28 percent. For weathered gasoline-containing soil samples, the bias was relatively independent of the TPH concentration range and exceeded the generally acceptable bias stated in SW-846 by up to 5 percentage points. For neat gasoline samples, the bias did not exceed the acceptable bias. For diesel-containing soil samples, the bias increased with decreases in the TPH concentration range, and the bias for low-, medium-, and high-range samples exceeded the acceptable bias by 29, 14, and 2 percentage points, respectively. For neat diesel samples, the observed positive bias did not exceed the acceptable bias. The low RSDs (5 to 9 percent) associated with the reference method indicated good precision in analyzing both soil and liquid samples. Collectively, these observations suggest that caution should be exercised during comparisons of PetroFLAG™ System and reference method results for low- and medium-range soil samples containing diesel.

6.3 Data Quality

Based on the reference method's performance in analyzing the QC check samples and selected PE samples, the reference method results were considered to be of adequate quality for the following reasons: (1) the reference method was implemented with acceptable accuracy (±30 percent) for all samples except low- and medium-concentration-range soil samples containing diesel, which made up only 13 percent of the total number of samples analyzed during the demonstration, and (2) the reference method was implemented with good precision for all samples (the overall RPD range was 0 to 17). The reference method results generally exhibited a negative bias. However, the bias was considered to be significant primarily for low- and medium-range soil samples containing diesel because the bias exceeded the generally acceptable bias of ±30 percent stated in SW-846 by 29 percentage points for low-range and 14 percentage points for medium-range samples. The reference method recoveries observed were typical of the recoveries obtained by most organic analytical methods for environmental samples.

Chapter 7
Performance of the PetroFLAG™ System

To verify a wide range of performance attributes, the demonstration had both primary and secondary objectives. Primary objectives were critical to the technology evaluation and were intended to produce quantitative results regarding a technology's performance. Secondary objectives provided information that was useful but did not necessarily produce quantitative results regarding a technology's performance. This chapter discusses the performance of the PetroFLAG™ System based on the primary objectives (excluding costs associated with TPH measurement) and secondary objectives. Costs associated with TPH measurement (primary objective P6) are presented in Chapter 8. The demonstration results for both the primary and secondary objectives are summarized in Chapter 9.

7.1 Primary Objectives

This section discusses the performance results for the PetroFLAG™ System based on primary objectives P1 through P5, which are listed below.

P1. Determine the MDL

P2. Evaluate the accuracy and precision of TPH measurement for a variety of contaminated soil samples

P3. Evaluate the effect of interferents on TPH measurement

P4. Evaluate the effect of soil moisture content on TPH measurement

P5. Measure the time required for TPH measurement

To address primary objectives P1 through P5, samples were collected from four different sampling areas. In addition, soil and liquid PE samples were prepared and distributed to Dexsil and the reference laboratory; of these samples, Dexsil chose not to analyze low- and medium-concentration-range weathered gasoline soil PE samples because according to Dexsil, the PetroFLAG™ System was not sensitive to weathered gasoline concentrations less than 1,000 mg/kg. In addition, Dexsil chose not to analyze soil samples collected in the PRA because Dexsil believed that the natural organic material in the area would adversely impact the PetroFLAG™ System's ability to accurately measure TPH. The numbers and types of environmental samples collected in each sampling area and the numbers and types of PE samples prepared are discussed in Chapter 4.

Primary objectives P1 through P4 were addressed using statistical and nonstatistical approaches, as appropriate. The statistical tests performed to address these objectives are illustrated in the flow diagram in Figure 7-1. Before a parametric test was performed, the Wilk-Shapiro test was used to determine whether the PetroFLAG™ System results and reference method results or, when appropriate, their differences were normally distributed at a significance level of 5 percent. If the results or their differences were not normally distributed, the Wilk-Shapiro test was performed on transformed results (for example, logarithm and square root transformations) to verify the normality assumption. If the normality assumption was not met, a nonparametric test was performed. Nonparametric tests are not as powerful as parametric tests because the nonparametric tests do not account for the magnitude of the difference between sample results. Despite this limitation, when the normality assumption was not met, performing a nonparametric test was considered to be a better alternative than performing no statistical comparison.

For the PetroFLAG™ System, when the TPH concentration in a given sample was reported as below the reporting limit, one-half the reporting limit was used as the

ure content
ive P4)

TPH concentration for that sample, as is commonly done, so that necessary calculations could be performed without rejecting the data. The same approach was used for the reference method except that the appropriate reporting limits were used in calculating the TPH concentration depending on which TPH measurement components (GRO, DRO, and ORO) were reported at concentrations below the reporting limits. In addition, for the PetroFLAG™ System, when the TPH concentration in a given sample was reported as a "greater than" value, the specified value was used as the TPH concentration for that sample so that necessary calculations could be performed without rejecting the data. Caution was exercised to ensure that these necessary data manipulations did not alter the conclusions.

The reference method GRO results were adjusted for solvent dilution associated with the soil sample moisture content because the method required use of methanol, a water-miscible solvent, for extraction of soil samples. Although the PetroFLAG™ System also required use of a water-miscible solvent for extraction of soil samples, the device's TPH results were not adjusted at the request of Dexsil. In addition, based on discussions with Dexsil, a given TPH result for the PetroFLAG™ System was rounded to the nearest integer when it was less than or equal to 99 mg/kg or 99 mg/L and to the nearest 10 when it was greater than 99 mg/kg or 99 mg/L. Similarly, based on discussions with the reference laboratory, all TPH results for the reference method were rounded to three significant figures.

7.1.1 Primary Objective P1: Method Detection Limit

To determine the MDLs for the PetroFLAG™ System and reference method, both Dexsil and the reference laboratory analyzed seven low-concentration-range soil PE samples containing diesel. Because the PetroFLAG™ System and reference method results were both normally distributed, the MDLs for the soil PE samples containing diesel were calculated using Equation 7-1 (40 CFR Part 136, Appendix B, Revision 1.1.1). An MDL thus calculated is influenced by TPH concentrations because the standard deviation will likely decrease with a decrease in TPH concentrations. As a result, the MDL will be lower when low-range samples are used for MDL determination. Despite this limitation, Equation 7-1 is commonly used and provides a reasonable estimate of the MDL.

$$MDL = (S)\, t_{(n-1,\, 1-\alpha=0.99)} \qquad (7\text{-}1)$$

where

S = Standard deviation of replicate TPH results

$t_{(n-1,1-\alpha=0.99)}$ = Student's t-value appropriate for a 99 percent confidence level and a standard deviation estimate with n-1 degrees of freedom (3.143 for n = 7 replicates)

Because GRO compounds were not expected to be present in the soil PE samples containing diesel, the reference laboratory performed only EDRO analysis of these samples and reported the sums of the DRO and ORO concentrations as the TPH results. The PetroFLAG™ System and reference method results for these samples are presented in Table 7-1.

Table 7-1. TPH Results for Low-Concentration-Range Diesel Soil Performance Evaluation Samples

	PetroFLAG™ System Result (mg/kg)	Reference Method Result (mg/kg)
	72	12.0
	61	16.5
	75	13.7
	68	16.4
	76	17.4
	80	17.2
	77	14.8
MDL	20	6.32

Notes:

MDL = Method detection limit
mg/kg = Milligram per kilogram

Based on the TPH results for the low-concentration-range diesel soil PE samples, the MDLs were determined to be 20 and 6.32 mg/kg for the PetroFLAG™ System and reference method, respectively. Because the ORO concentrations in all these samples were below the reference laboratory's estimated reporting limit (5.1 mg/kg), the MDL for the reference method was also calculated using only DRO results. The MDL for the reference method based on the DRO results was 6.29 mg/kg, whereas the MDL for the reference method based on the EDRO results was 6.32 mg/kg, indicating that the ORO concentrations below the reporting limit did not impact the MDL for the reference method.

The MDL of 20 mg/kg for the PetroFLAG™ System was greater than the MDL of 13 mg/kg claimed by Dexsil for soil samples containing diesel. The MDL of 6.32 mg/kg for the reference method compared well with the MDL of 4.72 mg/kg published in SW-846 Method 8015C for diesel samples extracted using a pressurized fluid extraction method and analyzed for DRO.

7.1.2 Primary Objective P2: Accuracy and Precision

This section discusses the ability of the PetroFLAG™ System to accurately and precisely measure TPH concentrations in a variety of contaminated soils. The PetroFLAG™ System TPH results were compared to the reference method TPH results. Accuracy and precision are discussed in Sections 7.1.2.1 and 7.1.2.2, respectively.

7.1.2.1 Accuracy

The accuracy of PetroFLAG™ System measurement of TPH was assessed by determining

- Whether the conclusion reached using the PetroFLAG™ System agreed with that reached using the reference method regarding whether the TPH concentration in a given sampling area or soil type exceeded a specified action level
- Whether the PetroFLAG™ System results were biased high or low compared to the reference method results
- Whether the PetroFLAG™ System results were different from the reference method results at a statistical significance level of 5 percent when a pairwise comparison was made
- Whether a significant correlation existed between the PetroFLAG™ System and reference method results

During examination of these four factors, the data quality of the reference method and PetroFLAG™ System TPH results was considered. For example, as discussed in Chapter 6, the reference method generally exhibited a low bias. However, the bias observed for all samples except low- and medium-concentration-range diesel soil samples did not exceed the generally acceptable bias of ±30 percent stated in SW-846 for organic analyses. Therefore, caution was exercised during comparison of the PetroFLAG™ System and reference method results, particularly those for low- and medium-range diesel soil samples. Caution was also exercised during interpretation of statistical test conclusions drawn based on a small number of samples. For example, only three samples were used for each type of PE sample except the low-range diesel samples; the small number of samples used increased the probability that the results being compared would be found to be statistically the same.

As discussed in Chapter 2, during the demonstration, the PetroFLAG™ System TPH results were determined using response factors that Dexsil considered to be appropriate for the PHCs suspected to be present in the demonstration samples. The two response factors used by Dexsil during the demonstration were 2 (for weathered gasoline) and 6 (for No. 6 fuel oil). Table 7-2 presents the response factors used for both soil and liquid demonstration samples. Although no demonstration samples contained No. 6 fuel oil, Dexsil used the response factor for No. 6 fuel oil instead of the diesel response factor so that the PetroFLAG™ System TPH results would agree with those of the reference method, which was known to have a negative bias. Based on the information provided to Dexsil regarding the types of PHCs suspected to be present in the samples provided, the response factors used seemed to be appropriate for some samples (for example, FFA samples) but not for others (samples containing MTBE and PCE). All PetroFLAG™ System TPH results presented in this ITVR are based on the response factors used by Dexsil during the demonstration. Dexsil's perspective on the selection of response factors is presented in the appendix.

The following sections discuss how the PetroFLAG™ System results compared with the reference method results by addressing each of the four factors identified above.

Action Level Conclusions

Table 7-3 compares action level conclusions reached using the PetroFLAG™ System and reference method results for environmental and soil PE samples. Section 4.2 of this ITVR explains how the action levels were selected for the demonstration. Of the environmental samples, the percentage of samples for which the conclusions agreed ranged from 60 to 88. Of the PE samples, the percentage of samples for which the conclusions agreed ranged from 33 to 100. Overall, the conclusions were the same for 73 percent of the samples.

Table 7-2. PetroFLAG™ System Response Factors

Sampling Area or Sample Type	Contamination Type	Response Factor Used[a]
Fuel Farm Area	Weathered diesel	6
Naval Exchange Service Station Area	Weathered gasoline	6
B-38 Area	Fresh gasoline and diesel or weathered gasoline and trace amounts of lubricating oil	6
Slop Fill Tank Area	Slightly weathered gasoline, kerosene, JP-5, and diesel	2
Soil performance evaluation samples	Weathered gasoline	2
	Weathered gasoline with interferents	2
	Diesel	6
	Diesel with interferents	6
	Blank	2
	Blank with humic acid	6
Liquid performance evaluation samples	Weathered gasoline	6
	Diesel	6
	Methyl-tert-butyl ether	6
	Tetrachloroethene	6
	Stoddard solvent	6
	Turpentine	6
	1,2,4-Trichlorobenzene	6

Note:

[a] The response factors of 2 and 6 correspond to weathered gasoline and No. 6 fuel oil, respectively, for the PetroFLAG™ System; the response factor for diesel is 5.

The least agreement observed for the environmental samples was for those from the FFA. This observation appeared to be associated with the significant negative bias observed for the reference method TPH results for low-concentration-range diesel soil PE samples discussed in Chapter 6.

The lack of agreement observed for two types of PE samples, blank soil and blank soil containing humic acid, appeared to be associated with the background reading, or noise, that the PetroFLAG™ System measured in blank soil, which was at least one order of magnitude greater than the concentrations reported by ERA, the PE sample provider. According to ERA, the blank soil samples used during the demonstration contain (1) less than 16 mg/kg of PHCs based on an infrared analysis and (2) less than 2 mg/kg of GRO and less than 10 mg/kg of DRO using a GC analysis (Tetra Tech 2001). Of the soil PE samples containing high-concentration-range weathered gasoline, the reference method results for the samples whose action level conclusions did not agree were within 5 percent of the action level, making it difficult to accurately assess whether the sample concentrations were above or below the action level. The lack of agreement observed for soil PE samples containing low-range diesel appeared to be associated with the significant negative bias of the reference method TPH results for such samples discussed in Chapter 6.

When the action level conclusions did not agree, the TPH results were further interpreted to assess whether the PetroFLAG™ System conclusion was conservative. The PetroFLAG™ System conclusion was considered to be conservative when the PetroFLAG™ System result was above the action level and the reference method result was below the action level. A regulatory agency would likely favor a field measurement device whose results are conservative; however, the party responsible for a site cleanup might not favor a device that is overly conservative because of the cost associated with unnecessary cleanup. Of the 26 PetroFLAG™ System action level conclusions that did not agree with the reference method conclusions, all 26 conclusions were conservative.

Table 7-3. Action Level Conclusions

Sampling Area or Sample Type		Action Level (mg/kg)	Total Number of Samples Analyzed	Percentage of Samples for Which PetroFLAG™ System and Reference Method Conclusions Agreed	When Conclusions Did Not Agree, Were PetroFLAG™ System Conclusions Conservative or Not Conservative?[a]
Fuel Farm Area		100	10	60	Conservative
Naval Exchange Service Station Area		50	20	75	
B-38 Area		100	8	88	
Slop Fill Tank Area		500	28	78	
PE sample	Blank soil (9 percent moisture content)	10	3	67	
PE sample	Blank soil and humic acid (9 percent moisture content)	200	6	50	
Soil PE sample containing weathered gasoline in	High-concentration range (9 percent moisture content)	2,000	3	67	
	High-concentration range (16 percent moisture content)	2,000	3	33	
Soil PE sample containing diesel in	Low-concentration range (9 percent moisture content)	15	7	57	
	Medium-concentration range (9 percent moisture content)	200	3	100	
	High-concentration range (less than 1 percent moisture content)	2,000	3	100	
	High-concentration range (9 percent moisture content)	2,000	3	100	
Total			97	73	

Notes:

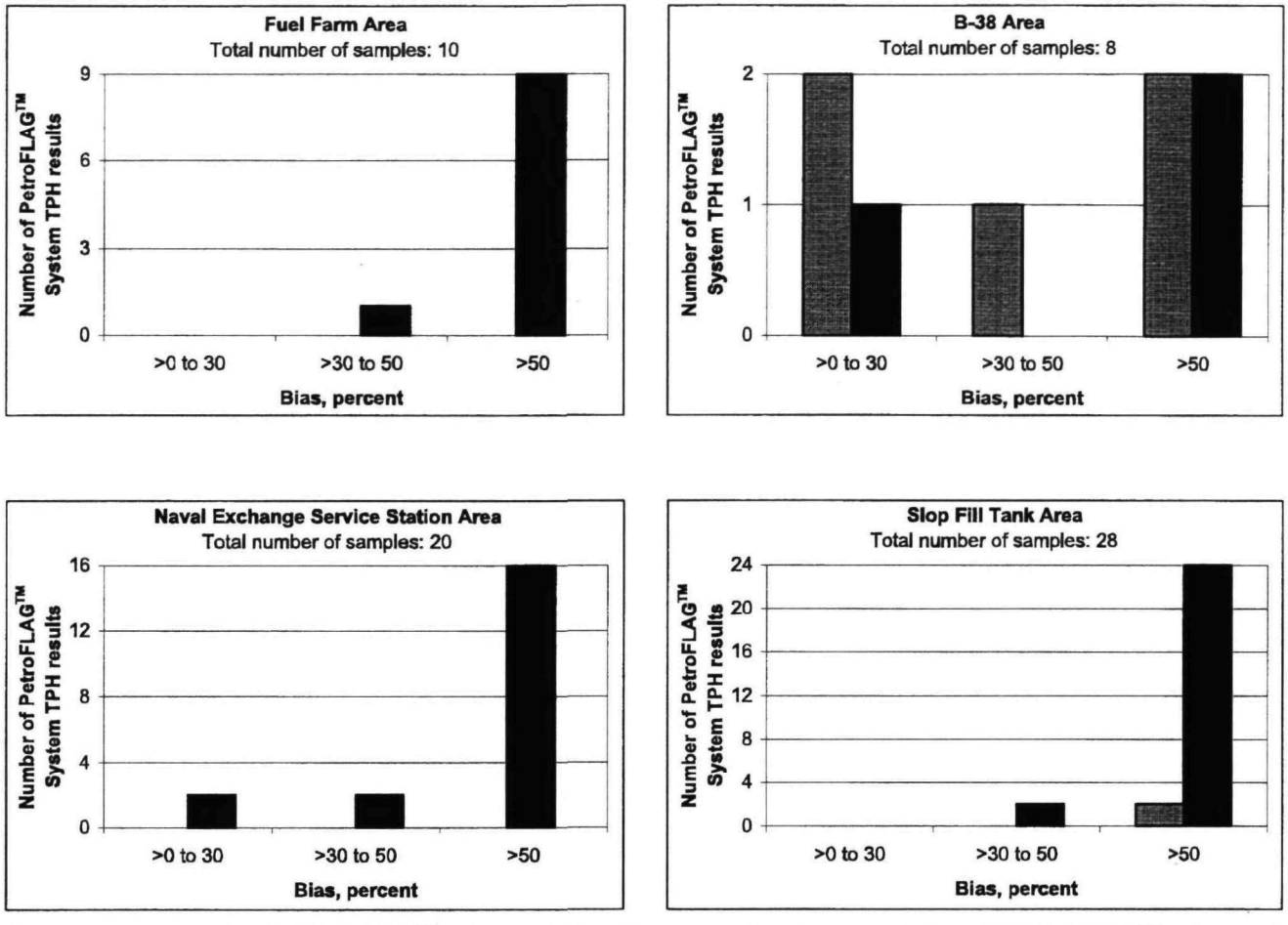
mg/kg = Milligram per kilogram
PE = Performance evaluation

[a] A conclusion was considered to be conservative when the PetroFLAG™ System result was above the action level and the reference method result was below the action level. A conservative conclusion may also be viewed as a false positive.

Measurement Bias

To determine the measurement bias, the ratios of the PetroFLAG™ System TPH results to the reference method TPH results were calculated. The observed bias values were grouped to identify the number of PetroFLAG™ System results within the following ranges of the reference method results: (1) greater than 0 to 30 percent, (2) greater than 30 to 50 percent, and (3) greater than 50 percent.

Figure 7-2 shows the distribution of measurement bias for the environmental samples. Of the four sampling areas, the best agreement between the PetroFLAG™ System and reference method results was observed for samples collected from the B-38 Area; for these samples, 50 percent of the PetroFLAG™ System results were within 50 percent of the reference method results. The percentages of samples whose device results were within 50 percent of the reference method results were significantly lower for the FFA (10 percent), NEX Service Station Area (20 percent), and SFT Area (7 percent). Measurement bias for the NEX Service Station Area was assessed using 3,330 mg/kg as the TPH result for the two PetroFLAG™ System results reported as greater than 3,330 mg/kg (see Table 7-4). As a result, the percent bias for the two samples may have actually been higher than calculated (30 percent). Excluding B-38 Area samples, the PetroFLAG™ System results for environmental samples were biased high except for 2 of 58 samples (3 percent). The high bias of these results could not be explained based solely on the negative bias associated with reference method TPH results. For example, for the SFT Area samples, some of the high bias observed was attributable to the response factor used in calculating the PetroFLAG™ System TPH results. The low bias observed for the B-38 Area samples was attributable to both the response factor used and the PetroFLAG™ System's lack of sensitivity to low-concentration-range weathered



Notes: > = Greater than; ▒ PetroFLAG™ system result biased low compared to reference method result; ■ PetroFLAG™ system result biased high compared to reference method result

Figure 7-2. Measurement bias for environmental samples.

gasoline. However, the high bias observed for the NEX Service Station Area samples could not be explained.

Figure 7-3 shows the distribution of measurement bias for selected soil PE samples. Of the four sets of samples containing PHCs and the one set of blank samples, good agreement between the PetroFLAG™ System and reference method results was observed for the high-concentration-range weathered gasoline and diesel samples. All PetroFLAG™ System results for the high-range diesel samples were within 30 percent of the reference method results. The PetroFLAG™ System results for three of the six high-range weathered gasoline samples were within 50 percent of the reference method results. The remaining PetroFLAG™ System results for soil PE samples, including blank samples, were biased high by greater than 50 percent. The high bias observed for the blank PE samples may have been associated with the background reading, or noise, that the PetroFLAG™ System measured in blank soil as discussed above under "Action Level Conclusions." The high bias observed for low-range diesel samples appeared to be associated with the significant negative bias of the reference method TPH results for such samples. The high bias of greater than 50 percent observed for the remaining samples cannot be explained based solely on the negative bias associated with the reference method.

Pairwise Comparison of TPH Results

To evaluate whether a statistically significant difference existed between the PetroFLAG™ System and reference

Table 7-4. Statistical Comparison of PetroFLAG™ System and Reference Method TPH Results for Environmental Samples

Sampling Area	TPH Result (mg/kg)		Statistical Analysis Summary		
	PetroFLAG™ System	Reference Method	Statistical Test and Null Hypothesis	Were PetroFLAG™ System and Reference Method Results Statistically the Same or Different?	Probability of Null Hypothesis Being True (percent)
Fuel Farm Area	320	68.2	Statistical Test Wilcoxon signed rank test (nonparametric) Null Hypothesis The median of the differences between the paired observations (PetroFLAG™ System and reference method results) is equal to zero.	Different	0.2
	25,000	15,000			
	280	90.2			
	24,500	12,000			
	300	44.1			
	19,500	13,900			
	3,240	1,330			
	13,570	8,090			
	230	93.7			
	23,200	12,300			
Naval Exchange Service Station Area	1,170	28.8	Statistical Test Two-tailed, paired Student's t-test (parametric) Null Hypothesis The mean of the differences between the paired observations (PetroFLAG™ System and reference method results) is equal to zero.	Different[a]	0.00
	630	144			
	1,550	617			
	460	293			
	830	280			
	>3,330	1,870			
	>3,330	1,560			
	850	9.56			
	750	270			
	2,040	881			
	1,860	1,120			
	740	14.2			
	1,080	219			
	1,610	1,180			
	1,860	1,390			
	470	15.2			
	530	54.5			
	>3,330	2,570			
	>3,330	3,030			
	910	15.9			
B-38 Area	23	79.0		Same	58.52
	44	41.5			
	39	61.4			
	26	67.3			
	150	193			
	130	69.4			
	36	43.8			
	92	51.6			

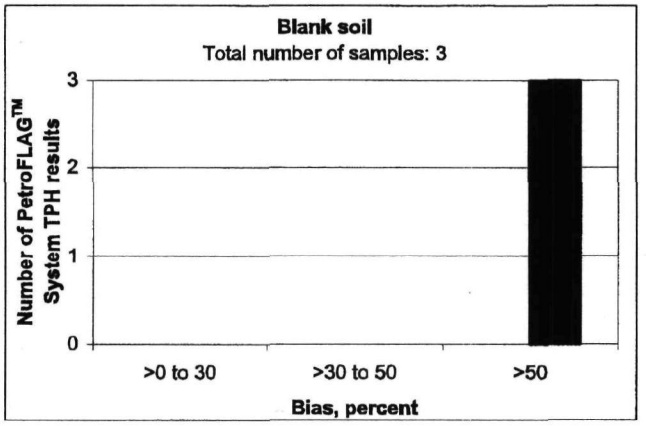
Table 7-4. Statistical Comparison of PetroFLAG™ System and Reference Method TPH Results for Environmental Samples (Continued)

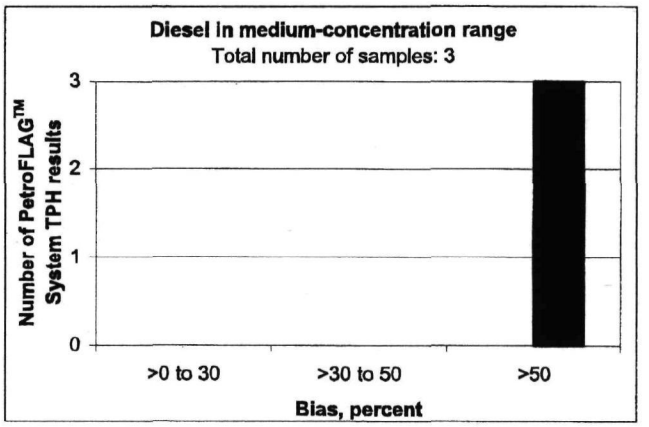
Sampling Area	TPH Result (mg/kg)		Statistical Analysis Summary		
	PetroFLAG™ System	Reference Method	Statistical Test and Null Hypothesis	Were PetroFLAG™ System and Reference Method Results Statistically the Same or Different?	Probability of Null Hypothesis Being True (percent)
Slop Fill Tank Area	610	105	Statistical Test Two-tailed, paired Student's t-test (parametric) Null Hypothesis The mean of the differences between the paired observations (PetroFLAG™ System and reference method results) is equal to zero.	Different	0.00
	470	269			
	1,030	397			
	580	339			
	110	6.16			
	83	37.1			
	100	43.9			
	250	52.4			
	6,980	3,300			
	2,100	1,270			
	1,570	588			
	1,070	554			
	1,410	834			
	870	501			
	960	280			
	460	185			
	2,360	1,090			
	760	544			
	860	503			
	360	146			
	1,510	938			
	830	517			
	1,170	369			
	340	253			
	2,140	151			
	15,260	3,960			
	580	1,210			
	56	121			

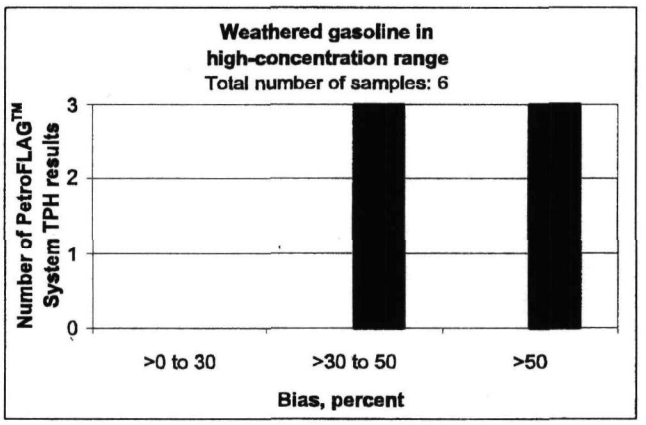
Notes:

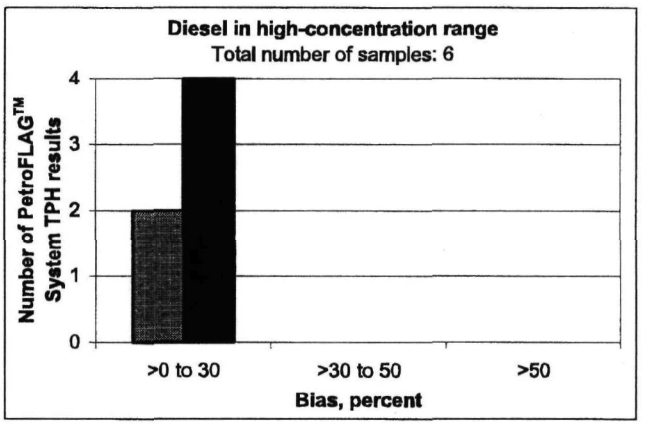
> = Greater than
mg/kg = Milligram per kilogram

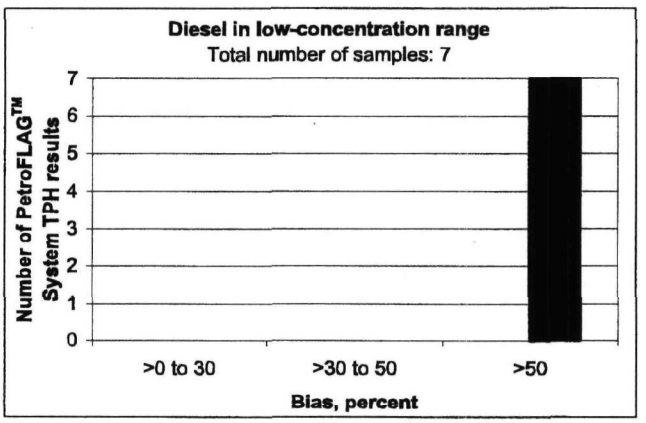
[a] When the PetroFLAG™ System results of >3,330 mg/kg were not included in the statistical analysis, a two-tailed, paired Student's t-test (parametric) showed that the PetroFLAG™ System and reference method results were still statistically different (the probability was 0.00 percent).











Notes:

> = Greater than

PetroFLAG™ system result biased low compared to reference method result

PetroFLAG™ system result biased high compared to reference method result

Figure 7-3. Measurement bias for soil performance evaluation samples.

method TPH results, a parametric test (a two-tailed, paired Student's t-test) or a nonparametric test (a Wilcoxon signed rank test) was selected based on the approach presented in Figure 7-1. Tables 7-4 and 7-5 present statistical comparisons of the PetroFLAG™ System and reference method results for environmental and PE samples, respectively. The tables present the PetroFLAG™ System and reference method results for each sampling area or PE sample type, the statistical test performed and the associated null hypothesis used to compare the results, whether the results were statistically the same or different, and the probability that the results were the same.

Table 7-4 shows that the PetroFLAG™ System and reference method results for all sampling areas except the B-38 Area were statistically different at a significance level of 5 percent. Specifically, the probability of the results being the same was less than 5 percent for the FFA, NEX Service Station Area, and SFT Area. The statistical test conclusions appeared to be reasonable because compared to the reference method results, the PetroFLAG™ System results were (1) biased high for the FFA samples by up to a factor of seven, (2) biased high for the NEX Service Station Area samples by up to two orders of magnitude, and (3) biased high for 26 SFT Area samples by up to a factor of 18 and biased low for 2 SFT Area samples by a factor of two. The pairwise comparison for the NEX Service Station Area was performed using 3,330 mg/kg as the TPH result for the four PetroFLAG™ System results reported as greater than 3,330 mg/kg. When the PetroFLAG™ System results of greater than 3,330 mg/kg were not included in the statistical analysis, the probability that the PetroFLAG™ System and reference method results were the same remained unchanged, indicating that the results were still statistically different.

Table 7-5 shows that the PetroFLAG™ System and reference method results were statistically the same at a significance level of 5 percent for high-concentration-range diesel soil PE samples. The PetroFLAG™ System and reference method results for all other PE sample types were statistically different. Of the PetroFLAG™ System results for PE samples that were statistically different from the reference method results, the PetroFLAG™ System results for (1) blank soil samples were biased high by at least an order of magnitude, (2) weathered gasoline soil samples and medium-range soil diesel soil samples were biased high by up to a factor of two, (3) low-range diesel soil samples were biased high by up to a factor of six, and (4) liquid samples were biased low by up to 71 percent for neat weathered gasoline and by up to 30 percent for neat diesel. In addition, the PetroFLAG™ System results for the liquid PE samples were biased low when compared to the sample densities; specifically, the PetroFLAG™ System results were biased low by 76 percent for neat weathered gasoline and by 8 percent for neat diesel. The low bias observed for neat weathered gasoline was largely associated with the response factor selected by Dexsil for neat weathered gasoline samples. Specifically, had Dexsil selected the response factor for weathered gasoline (2) instead of the response factor used for diesel samples during the demonstration (6), the device results for neat weathered gasoline samples would have been three times higher; moreover, the bias would have been reduced to 34 percent when the device results were compared to the sample density and to 8 percent when the device results were compared to the average TPH results of the reference method.

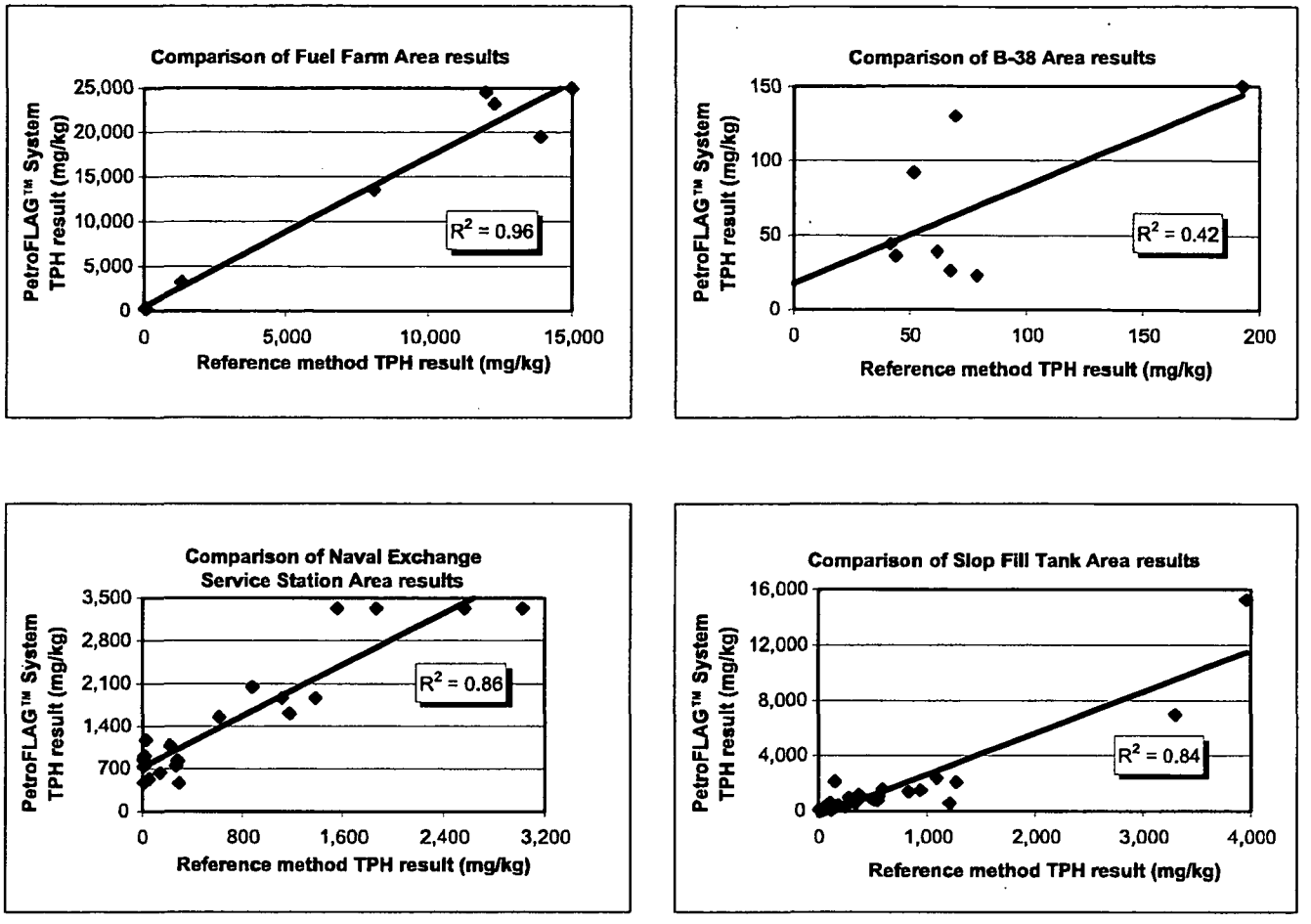
Correlation of TPH Results

To determine whether a significant correlation existed between the PetroFLAG™ System and reference method TPH results, linear regression analysis was performed. A strong correlation between the PetroFLAG™ System and reference method results would indicate that the device results could be adjusted using the established correlation and that field decisions could be made using the adjusted results in situations where the device results may not be the same as off-site laboratory results. Figures 7-4 and 7-5 show the linear regression plots for environmental and soil PE samples, respectively. Table 7-6 presents the regression model, square of the correlation coefficient (R^2), and probability that the slope of the regression line is equal to zero (F-test probability) for each sampling area and soil PE sample type. Because Dexsil chose to analyze only the high-concentration-range samples during the demonstration, the range of corresponding reference method TPH results was small (1,740 to 2,180 mg/kg). Therefore, the regression analysis for weathered gasoline samples was less robust than that for other samples.

Table 7-6 shows that R^2 values for (1) environmental samples except B-38 Area samples ranged from 0.84 to 0.96 and (2) soil PE samples except weathered gasoline samples were at least 0.89. The R^2 values were considerably lower for B-38 Area samples (0.42) and weathered gasoline soil PE samples (0.10). The linear regression analysis for the NEX Service Station Area was conducted using 3,330 mg/kg for the four PetroFLAG™

Table 7-5. Statistical Comparison of PetroFLAG™ System and Reference Method TPH Results for Performance Evaluation Samples

Sample Type		TPH Result: PetroFLAG™ System	TPH Result: Reference Method	Statistical Analysis Summary: Statistical Test and Null Hypothesis	Statistical Analysis Summary: Were PetroFLAG™ System and Reference Method Results Statistically the Same or Different?	Statistical Analysis Summary: Probability of Null Hypothesis Being True (percent)
Soil Samples (Processed Garden Soil) (TPH Results in Milligram per Kilogram)						
Blank (9 percent moisture content)		170	5.12	Statistical Test Two-tailed, paired Student's t-test (parametric) Null Hypothesis The mean of the differences between the paired observations (PetroFLAG™ System and reference method results) is equal to zero.	Different	0.11
		160	13.1			
		170	13.5			
Weathered gasoline	High-concentration range (9 percent moisture content)	3,760	1,880		Different	1.67
		3,650	2,020			
		3,360	2,180			
	High-concentration range (16 percent moisture content)	2,550	1,740		Different	0.78
		2,920	1,980			
		2,740	2,050			
Diesel	Low-concentration range (9 percent moisture content)	72	12.0		Different	0.00
		61	16.5			
		75	13.7			
		68	16.4			
		76	17.4			
		80	17.2			
		77	14.8			
	Medium-concentration range (9 percent moisture content)	510	226		Different	0.11
		530	265			
		520	267			
	High-concentration range (9 percent moisture content)	2,970	2,480		Same	29.33
		2,860	2,890			
		2,980	2,800			
	High-concentration range (less than 1 percent moisture content)	3,310	2,700		Same	22.19
		3,490	2,950			
		3,020	3,070			
Liquid Samples (Neat Materials) (TPH Results in Milligram per Liter)						
Weathered gasoline		213,860	656,000	Statistical Test Two-tailed, paired Student's t-test (parametric) Null Hypothesis The mean of the differences between the paired observations (PetroFLAG™ System and reference method results) is equal to zero.	Different	0.09
		178,890	611,000			
		200,200	677,000			
Diesel		783,900	1,090,000		Different	0.70
		763,000	1,020,000			
		815,260	1,160,000			



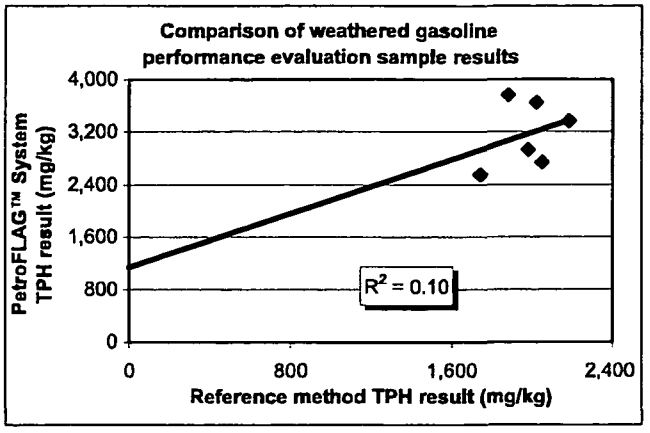
Notes:

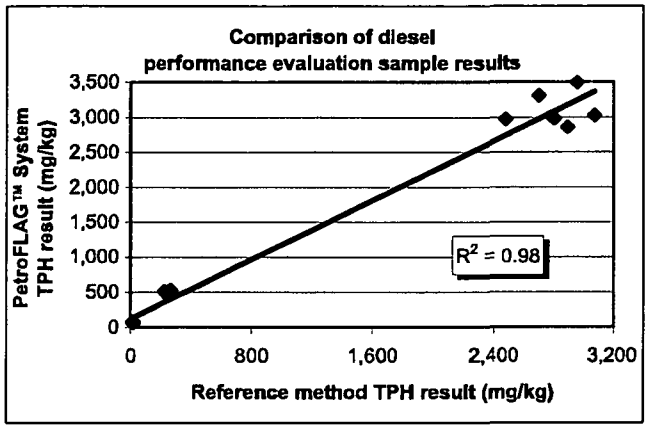
mg/kg = Milligram per kilogram R^2 = Square of the correlation coefficient

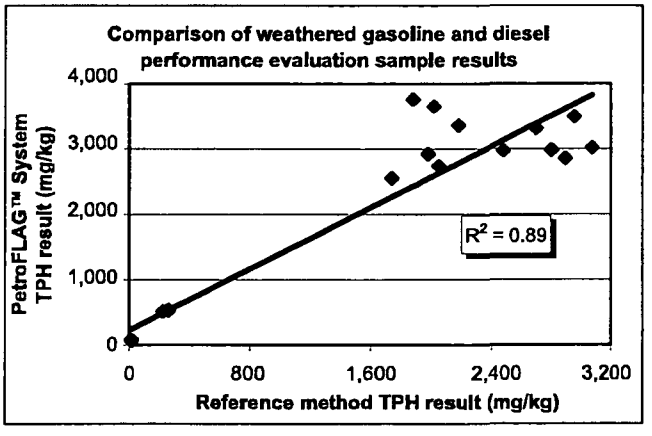
Figure 7-4. Linear regression plots for environmental samples.

System results reported as greater than 3,330 mg/kg. When the PetroFLAG™ System results of greater than 3,330 mg/kg were not included in the linear regression analysis, the R^2 value for this area decreased to 0.73. The R^2 value for the regression model for diesel soil PE samples (0.98) was significantly higher than that for weathered gasoline soil PE samples (0.10); therefore, it was not surprising that the R^2 value for the combined regression model for these PE samples was 0.89.

The probability of the slopes of the regression lines being equal to zero was 0.00 percent for all environmental and soil PE samples except B-38 Area and weathered gasoline soil PE samples, indicating that there was less than a 5 percent probability that the PetroFLAG™ System and reference method results correlated only by chance. The probability that the PetroFLAG™ System and reference method results correlated by chance was higher for B-38 Area samples (8.14 percent) and weathered gasoline soil PE samples (55.03 percent). Based on the R^2 and probability values, the PetroFLAG™ System and reference method results were considered to be (1) highly correlated for FFA samples, diesel soil PE samples, and weathered gasoline and diesel soil PE samples; (2) moderately correlated for NEX Service Station Area and SFT Area samples; and (3) weakly correlated for B-38 Area samples and weathered gasoline soil PE samples.







Notes:

mg/kg = Milligram per kilogram

R^2 = Square of the correlation coefficient

Figure 7-5. Linear regression plots for soil performance evaluation samples.

7.1.2.2 Precision

Both environmental and PE samples were analyzed to evaluate the precision associated with TPH measurements using the PetroFLAG™ System and reference method. The results of this evaluation are summarized below.

Environmental Samples

Blind field triplicates were analyzed to evaluate the overall precision of the sampling, extraction, and analysis steps associated with TPH measurement. Each set of field triplicates was collected from a well-homogenized sample. Also, extract duplicates were analyzed to evaluate analytical precision only. Each set of extract duplicates was collected by extracting a given soil sample and collecting two aliquots of the extract. Additional information on field triplicate and extract duplicate preparation is included in Chapter 4.

Tables 7-7 and 7-8 present the PetroFLAG™ System and reference method results for field triplicates and extract duplicates, respectively. Precision was estimated using RSDs for field triplicates and RPDs for extract duplicates.

Table 7-7 presents the TPH results and RSDs for 11 sets of field triplicates analyzed using the PetroFLAG™ System and reference method. For the PetroFLAG™ System, the RSDs ranged from 7 to 38 percent with a median of 19 percent. The RSDs for the reference method ranged from 4 to 39 percent with a median of 16 percent. The median RSDs for the PetroFLAG™ System and reference method indicated about the same level of precision. The PetroFLAG™ System and reference method RSDs did not exhibit consistent trends based on soil type, PHC contamination type, or TPH concentration.

Table 7-8 presents the TPH results and RPDs for 10 and 12 sets of extract duplicates analyzed using the PetroFLAG™ System and reference method, respectively. For the PetroFLAG™ System, the RPDs ranged from 1 to 26 with a median of 5. The RPDs for the reference method ranged from 0 to 11 with a median of 4. The median RPDs for the PetroFLAG™ System and reference method indicated about the same level of precision. The PetroFLAG™ System and reference method RPDs did not exhibit consistent trends based on PHC contamination type or TPH concentration. As expected, the median RPDs for extract duplicates were less than the median RSDs for field triplicates for both the PetroFLAG™ System and reference method. These findings indicated that greater

Table 7-6. Summary of Linear Regression Analysis Results

Sampling Area or Sample Type	Regression Model (y = PetroFLAG™ System TPH result, x = reference method TPH result)	Square of Correlation Coefficient	Probability That Slope of Regression Line Was Equal to Zero (percent)
Environmental Samples			
Fuel Farm Area	y = 1.68x + 444.10	0.96	0.00
Naval Exchange Service Station Area[a]	y = 1.06x + 711.08	0.86	0.00
B-38 Area	y = 0.66x + 17.48	0.42	8.14
Slop Fill Tank Area	y = 2.99x - 382.22	0.84	0.00
Soil Performance Evaluation Samples			
Weathered gasoline[b]	y = 1.02x + 1,140.67	0.10	55.03
Diesel	y = 1.06x + 118.68	0.98	0.00
Weathered gasoline and diesel	y = 1.17x + 225.73	0.89	0.00

Notes:

mg/kg = Milligram per kilogram

[a] The linear regression analysis for the Naval Exchange Service Station Area was conducted using 3,330 mg/kg for the four PetroFLAG™ System results reported as greater than 3,330 mg/kg. When the PetroFLAG™ System results of greater than 3,330 mg/kg were not included in the linear regression analysis, the square of the correlation coefficient value for this area decreased to 0.73, but the probability that the slope of the regression line was equal to zero remained the same.

[b] Because Dexsil chose to analyze only the high-concentration-range samples during the demonstration, the range of corresponding reference method TPH results was small (1,740 to 2,180 mg/kg). Therefore, the regression analysis for weathered gasoline samples was less robust than that for other samples.

precision was achieved when only the analysis step could have contributed to TPH measurement error than when all three steps (sampling, extraction, and analysis) could have contributed to such error.

Performance Evaluation Samples

Table 7-9 presents the PetroFLAG™ System and reference method TPH results and RSDs for seven sets of replicates for soil PE samples and two sets of triplicates for liquid PE samples. The PetroFLAG™ System RSDs for the replicate sets of soil samples ranged from 2 to 9 percent with a median of 6 percent. The PetroFLAG™ System RSDs for the two triplicate sets of liquid samples were 3 and 9 percent with a median of 6 percent.

For the reference method, the RSD calculated for the blank soil samples was not considered in evaluating the method's precision because one of the three blank soil sample results (5.12 mg/kg) was estimated by adding one-half the reporting limits for the GRO, DRO, and ORO components of TPH measurement. The RSDs for the remaining six replicate sets ranged from 6 to 13 percent with a median of 8 percent. The RSDs for the two triplicate sets of liquid samples were 5 and 6 percent with a median of 5.5 percent. The median RSDs for the PetroFLAG™ System and reference method indicated about the same level of precision. Finally, for the reference method, the median RSD for the soil PE samples (8 percent) was less than that for the environmental samples (16 percent), indicating that greater precision was achieved for the samples prepared under more controlled conditions (the PE samples). Similarly for the PetroFLAG™ System, the median RSD for soil PE samples (6 percent) was less than that for the environmental samples (19 percent).

7.1.3 Primary Objective P3: Effect of Interferents

The effect of interferents on TPH measurement using the PetroFLAG™ System and reference method was evaluated through analysis of high-concentration-range soil PE samples that contained weathered gasoline or diesel with or without an interferent. The six interferents used were MTBE; PCE; Stoddard solvent; turpentine; 1,2,4-trichlorobenzene; and humic acid. In addition, neat (liquid) samples of each interferent except humic acid were used as quasi-control samples to evaluate the effect of each interferent on the TPH results obtained using the PetroFLAG™ System and the reference method. Liquid interferent samples were submitted for analysis as blind

Table 7-7. Summary of PetroFLAG™ System and Reference Method Precision for Field Triplicates of Environmental Samples

Sampling Area	Field Triplicate Set	PetroFLAG™ System		Reference Method	
		TPH Result (milligram per kilogram)	Relative Standard Deviation (percent)	TPH Result (milligram per kilogram)	Relative Standard Deviation (percent)
Fuel Farm Area	1	320	7	68.2	34
		280		90.2	
		300		44.1	
	2	25,000	13	15,000	11
		24,500		12,000	
		19,500		13,900	
Naval Exchange Service Station Area	3	830	19	280	13
		750		270	
		1,080		219	
	4	>3,330	38[a]	1,870	39
		2,040		881	
		1,610		1,180	
	5	>3,330	36[a]	1,560	16
		1,860		1,120	
		1,860		1,390	
	6	850	28	9.56	23
		740		14.2	
		470		15.2	
B-38 Area	7	23	29	79	13
		39		61.4	
		26		67.3	
Slop Fill Tank Area	8	1,410	30	834	14
		2,360		1,090	
		1,510		938	
	9	870	7	501	4
		760		544	
		830		517	
	10	960	16	280	29
		860		503	
		1,170		369	
	11	460	16	185	28
		360		146	
		340		253	

Notes:

> = Greater than

[a] The relative standard deviations were calculated for triplicate sets 4 and 5 using 3,330 milligrams per kilogram for the PetroFLAG™ System results reported as >3,330 milligrams per kilogram.

Table 7-8. Summary of PetroFLAG™ System and Reference Method Precision for Extract Duplicates

Sampling Area	Extract Duplicate Set	PetroFLAG™ System		Reference Method	
		TPH Result (milligram per kilogram)	Relative Percent Difference	TPH Result (milligram per kilogram)	Relative Percent Difference
Fuel Farm Area	1	300	Not calculated[a]	44.1	0
		Not analyzed[a]		44.1	
	2	20,500	10	13,700	2
		18,500		14,000	
Naval Exchange Service Station Area	3	1,030	9	226	6
		1,130		213	
	4	1,550	7	1,190	2
		1,660		1,170	
	5	1,820	4	1,420	4
		1,900		1,360	
	6	470	Not calculated[a]	15.5	4
		Not analyzed[a]		14.9	
B-38 Area	7	20	26	79.6	2
		26		78.4	
	8	43	5	41.4	0
		45		41.5	
Slop Fill Tank Area	9	1,400	1	829	1
		1,420		838	
	10	850	5	528	11
		890		473	
	11	970	2	271	6
		950		289	
	12	450	2	189	4
		460		181	

Note:

[a] Not enough extract was generated to analyze the extract duplicate; therefore, a relative percent difference could not be calculated for this extract duplicate set.

triplicate samples. Dexsil and the reference laboratory were provided with flame-sealed ampules of each interferent and were given specific instructions to prepare dilutions of the liquid interferents for analysis. Two dilutions of each interferent were prepared; therefore, there were six PetroFLAG™ System and reference method TPH results for each interferent. Blank soil was mixed with humic acid at two levels to prepare quasi-control samples for this interferent. Additional details regarding the interferents are provided in Chapter 4. The results for the quasi-control interferent samples are discussed first below, followed by the effects of the interferents on the TPH results for soil samples.

7.1.3.1 Interferent Sample Results

Table 7-10 presents the PetroFLAG™ System and reference method TPH results, mean TPH results, and mean responses for triplicate sets of liquid PE samples and soil PE samples containing humic acid. Each mean response was calculated by dividing the mean TPH result for a triplicate set by the interferent concentration and multiplying by 100. For liquid PE samples, the interferent concentration was estimated using its density and purity.

The mean responses for the PetroFLAG™ System ranged from 0 to 103 percent for the liquid interferent samples; the mean response for humic acid was 2.5 percent. The

Table 7-9. Comparison of PetroFLAG™ System and Reference Method Precision for Replicate Performance Evaluation Samples

Sample Type		Replicate Set	PetroFLAG™ System		Reference Method	
			TPH Result	Relative Standard Deviation (percent)	TPH Result	Relative Standard Deviation (percent)
Soil Samples (Processed Garden Soil) (TPH Results in Milligram per Kilogram):						
Blank (9 percent moisture content)		1	170	3	5.12	45
			160		13.1	
			170		13.5	
Weathered gasoline	High-range TPH concentration (9 percent moisture content)	2	3,760	6	1,880	7
			3,650		2,020	
			3,360		2,180	
	High-range TPH concentration (16 percent moisture content)	3	2,550	7	1,740	8
			2,920		1,980	
			2,740		2,050	
Diesel	Low-range TPH concentration (9 percent moisture content)	4	72	9	12.0	13
			61		16.5	
			75		13.7	
			68		16.4	
			76		17.4	
			80		17.2	
			77		14.8	
	Medium-range TPH concentration (9 percent moisture content)	5	510	2	226	9
			530		265	
			520		267	
	High-range TPH concentration (9 percent moisture content)	6	2,970	2	2,480	8
			2,860		2,890	
			2,980		2,800	
	High-range TPH concentration (less than 1 percent moisture content)	7	3,310	7	2,700	6
			3,490		2,950	
			3,020		3,070	
Liquid Samples (Neat Materials) (TPH Results in Milligram per Liter):						
Weathered gasoline		8	213,860	9	656,000	5
			178,890		611,000	
			200,200		677,000	
Diesel		9	783,900	3	1,090,000	6
			763,000		1,020,000	
			815,260		1,160,000	

Table 7-10. Comparison of PetroFLAG™ System and Reference Method Results for Interferent Samples

Interferent and Concentration[a]	PetroFLAG™ System			Reference Method		
	TPH Result	Mean TPH Result	Mean Response[b] (percent)	TPH Result	Mean TPH Result	Mean Response[b] (percent)
Liquid Interferent Samples (TPH Results in Milligram per Liter)						
Methyl-tert-butyl ether (740,000 milligrams per liter)	<4,020	3,010	0	309,000	284,000	38
	<10,020			272,000		
	<4,020			270,000		
	<2,020	2,340	0	303,000	299,000	40
	<10, 020			313,000		
	<2,020			282,000		
Tetrachloroethene (1,621,000 milligrams per liter)	42,110	29,840	2	269,000	272,000	17
	12,530			270,000		
	34,890			277,000		
	>669,930	235,550	14[c]	290,000	295,000	18
	18,540			288,000		
	18,180			307,000		
Stoddard solvent (771,500 milligrams per liter)	329,660	334,330	43	561,000	598,000	78
	332,660			628,000		
	340,680			606,000		
	337,670	327,300	42	703,000	708,000	92
	332,140			Not reported		
	322,140			713,000		
Turpentine (845,600 milligrams per liter)	874,250	861,220	102	504,000	468,000	55
	844,690			459,000		
	864,730			442,000		
	880,260	877,250	104	523,000	408,000	48
	897,790			353,000		
	853,700			349,000		
1,2,4-Trichlorobenzene (1,439,000 milligrams per liter)	129,920	116,560	8	711,000	688,000	48
	128,320			620,000		
	91,430			732,000		
	462,510	342,630	24	754,000	754,000	52
	127,170			756,000		
	438,210			752,000		
Interferent Samples (Processed Garden Soil) (TPH Results in Milligram per Kilogram)						
Humic acid at 3,940 milligrams per kilogram	120	120	3	8.99	9.00	0
	110			8.96		
	140			8.12		
Humic acid at 19,500 milligrams per kilogram	410	380	2	69.3	76.0	0
	350			79.1		
	390			78.5		

Notes:

> = Greater than
< = Less than

[a] A given liquid interferent concentration was estimated using its density and purity.

[b] The mean response was calculated by dividing the mean TPH result for a triplicate set by the interferent concentration and multiplying by 100.

[c] When the PetroFLAG™ System result of >669,930 milligrams per liter (an analytical outlier) was not considered, the mean response was calculated to be 1 percent.

TPH results for a given triplicate set and between the triplicate sets showed good agreement for Stoddard solvent and turpentine. The mean responses for MTBE (0 percent) and Stoddard solvent (42.5 percent) indicated that Stoddard solvent can be measured as TPH using the device. The mean responses for turpentine (103 percent) and 1,2,4-trichlorobenzene (16 percent) indicated that both of these interferents will likely result in false positives during TPH measurement. The mean response for PCE (8 percent) was affected by one of the six high-level samples that had a TPH result (greater than 669,930 mg/L) up to an order of magnitude greater than the other five results, making the mean response questionable. When the PetroFLAG™ System result of greater than 669,930 mg/L (an analytical outlier) was not considered, the mean response for PCE (1.5 percent) indicated that this interferent would not result in either false positives or false negatives during TPH measurement. Also, the mean response of 2.5 percent for humic acid indicated that humic acid would not result in either false positives or false negatives during TPH measurement.

The mean responses for the reference method ranged from 17 to 92 percent for the liquid interferent samples; the mean response for humic acid was 0 percent. The TPH results for a given triplicate set and between the triplicate sets showed good agreement. The mean responses for MTBE (39 percent) and Stoddard solvent (85 percent) indicated that these compounds can be measured as TPH using the reference method. The mean responses for PCE (17.5 percent); turpentine (52 percent); and 1,2,4-trichlorobenzene (50 percent) indicated that these interferents will likely result in false positives during TPH measurement. The mean response of 0 percent for humic acid indicated that humic acid would not result in either false positives or false negatives during TPH measurement.

7.1.3.2 Effects of Interferents on TPH Results for Soil Samples

The effects of interferents on TPH measurement for soil samples containing weathered gasoline or diesel were examined through analysis of PE samples containing (1) weathered gasoline or diesel (control) and (2) weathered gasoline or diesel plus a given interferent at two levels. Information on the selection of interferents is provided in Chapter 4.

Triplicate sets of control samples and samples containing interferents were prepared for analysis using the PetroFLAG™ System and reference method. A parametric or nonparametric test was selected for statistical evaluation of the results using the approach presented in Figure 7-1.

TPH results for samples with and without interferents, statistical tests performed, and statistical test conclusions for both the PetroFLAG™ System and reference method are presented in Table 7-11. The null hypothesis for the statistical tests was that mean TPH results for samples with and without interferents were equal. The statistical results for each interferent are discussed below.

Effect of Methyl-Tert-Butyl Ether

The effect of MTBE was evaluated for soil PE samples containing weathered gasoline. Based on the liquid PE sample (neat material) analytical results, MTBE was expected to have no effect on the TPH results for the PetroFLAG™ System; however, it was expected to bias the reference method results high.

For the PetroFLAG™ System, MTBE biased the TPH results low; the bias was statistically significant only at the high MTBE level. This observation appeared to contradict the conclusions drawn from the analytical results for liquid PE samples containing MTBE (quasi-control samples); however, the apparent contradiction was attributable to the fact that the quasi-control sample analyses could predict only a positive bias (a negative bias is equivalent to a negative concentration).

For the reference method, at the interferent levels used, MTBE was expected to bias the TPH results high by 21 percent (low level) and 33 percent (high level). The expected bias would be lower (17 and 27 percent, respectively) if MTBE in soil samples was assumed to be extracted as efficiently as weathered gasoline in soil samples. However, no effect on TPH measurement was observed for soil PE samples analyzed during the demonstration. A significant amount of MTBE, a highly volatile compound, may have been lost during PE sample preparation, transport, storage, and handling, thus lowering the MTBE concentrations to levels that would not have increased the TPH results beyond the reference method's precision (7 percent).

Table 7-11. Comparison of PetroFLAG™ System and Reference Method Results for Soil Performance Evaluation Samples Containing Interferents

Sample Matrix and Interferent[a]		PetroFLAG™ System					Reference Method				
		TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)	TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)
Soil Samples Without Interferents											
Weathered gasoline		3,760	3,590	Not applicable			1,880	2,030	Not applicable		
		3,650					2,020				
		3,360					2,180				
Diesel		2,970	2,940	Not applicable			2,480	2,720	Not applicable		
		2,860					2,890				
		2,980					2,800				
Soil Samples With Interferents											
Weathered gasoline	MTBE (1,100 mg/kg)	3,140	3,360	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	Mean with interferent at high level was different from means without interferent and with interferent at low level	0.07	1,900	1,950	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	Same	11.21
		3,280					1,750				
		3,670					2,210				
	MTBE (1,700 mg/kg)	2,390	2,090				2,150	2,340			
		2,040					2,320				
		1,840					2,560				
	PCE (2,810 mg/kg)	4,570	6,100	Kruskal-Wallis one-way analysis of variance (nonparametric) and Kruskal-Wallis pairwise comparison of means (nonparametric)	Same	30.12[b]	2,540	2,380		Mean with interferent at high level was different from means without interferent and with interferent at low level	0.00
		5,960					2,160				
		7,780					2,450				
	PCE (13,100 mg/kg)	>20,000	8,530				4,740	4,450			
		2,890					4,570				
		2,690					4,040				

Table 7-11. Comparison of PetroFLAG™ System and Reference Method Results for Soil Performance Evaluation Samples Containing Interferents (Continued)

Sample Matrix and Interferent[a]		PetroFLAG™ System					Reference Method				
		TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)	TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)
Soil Samples With Interferents (Continued)											
Weathered gasoline (Continued)	Stoddard solvent (2,900 mg/kg)	8,410	7,200	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	All three means (with and without interferents) were significantly different from one another	0.02	4,350	4,410	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	All three means (with and without interferents) were significantly different from one another	0.00
		6,120					4,760				
		7,080					4,110				
	Stoddard solvent (15,400 mg/kg)	15,930	25,140				10,300	11,900			
		32,780					14,300				
		26,720					11,000				
Diesel	Stoddard solvent (3,650 mg/kg)	20,850	18,920		All three means (with and without interferents) were significantly different from one another	0.00	4,390	4,520		All three means (with and without interferents) were significantly different from one another	0.00
		18,860					4,640				
		17,040					4,520				
	Stoddard solvent (18,200 mg/kg)	39,300	31,680				8,770	7,880			
		28,670					6,580				
		27,080					8,280				
Weathered gasoline	Turpentine (2,730 mg/kg)	10,440	8,210		All three means (with and without interferents) were significantly different from one another	0.00[c]	4,410	4,240		All three means (with and without interferents) were significantly different from one another	0.00
		6,630					3,870				
		7,560					4,440				
	Turpentine (12,900 mg/kg)	58,200	70,020				12,800	12,900			
		51,870					11,200				
		>100,000					14,600				

Table 7-11. Comparison of PetroFLAG™ System and Reference Method Results for Soil Performance Evaluation Samples Containing Interferents (Continued)

Sample Matrix and Interferent[a]		PetroFLAG™ System					Reference Method				
		TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)	TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)
Soil Samples With Interferents (Continued)											
Diesel	Turpentine (3,850 mg/kg)	17,430	18,310	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	All three means (with and without interferents) were significantly different from one another	0.00	5,860	5,760	Kruskal-Wallis one-way analysis of variance (nonparametric) and Kruskal-Wallis pairwise comparison of means (nonparametric)	Mean without interferent was same as mean with interferent at low level; mean with interferent at low level was same as mean with interferent at high level	2.65
		17,040					5,810				
		20,470					5,610				
	Turpentine (19,600 mg/kg)	62,700	53,330				15,000	13,900			
		51,980					13,300				
		45,300					13,300				
	1,2,4-Trichloro-benzene (3,350 mg/kg)	3,770	3,890		All three means (with and without interferents) were significantly different from one another	0.00	3,220	3,510	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	Mean with interferent at high level was different from means without interferent and with interferent at low level	0.01
		3,990					3,750				
		3,900					3,550				
	1,2,4-Trichloro-benzene (16,600 mg/kg)	10,100	9,520				7,940	7,060			
		8,550					6,560				
		9,920					6,690				

Table 7-11. Comparison of PetroFLAG™ System and Reference Method Results for Soil Performance Evaluation Samples Containing Interferents (Continued)

Sample Matrix and Interferent[a]		PetroFLAG™ System					Reference Method				
		TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)	TPH Result (mg/kg)	Mean TPH Result (mg/kg)	Statistical Tests	Were Mean TPH Results for Samples With and Without Interferents the Same or Different?	Probability of Mean TPH Results for Samples With and Without Interferents Being the Same (percent)
Soil Samples With Interferents (Continued)											
Diesel (Continued)	Humic acid (3,940 mg/kg)	2,870	2,800	Kruskal-Wallis one-way analysis of variance (nonparametric) and Kruskal-Wallis pairwise comparison of means (nonparametric)	Same	39.32	2,150	2,200	One-way analysis of variance (parametric) and Tukey (honest, significant difference) pairwise comparison of means (parametric)	Mean without interferent was same as mean with interferent at high level; mean with interferent at low level was same as mean with interferent at high level	3.87
		2,880					2,080				
		2,660					2,360				
	Humic acid (19,500 mg/kg)	3,140	2,990				2,660	2,450			
		2,680					2,420				
		3,150					2,270				

Notes:

> = Greater than
mg/kg = Milligram per kilogram
MTBE = Methyl-tert-butyl ether
PCE = Tetrachloroethene

[a] All samples were prepared at a 9 percent moisture level.

[b] When the PetroFLAG™ System result of >20,000 mg/kg (an analytical outlier) was not considered, a Kruskal-Wallis one-way analysis of variance (nonparametric) and a Kruskal-Wallis pairwise comparison of means (nonparametric) showed that the mean without the interferent was the same as the means with the interferent at the low and high levels; however, the mean with the interferent at the low level was not the same as the mean with the interferent at the high level. The probability of mean TPH results for samples with and without interferents being the same was 4.39 percent.

[c] When the PetroFLAG™ System result of >100,000 mg/kg (an analytical outlier) was not considered, a Kruskal-Wallis one-way analysis of variance (nonparametric) and a Kruskal-Wallis pairwise comparison of means (nonparametric) showed that the mean without the interferent was the same as the mean with the interferent at the low level and that the mean with the interferent at the low level was the same as the mean with the interferent at the high level. The probability of mean TPH results for samples with and without interferents being the same was 4.39 percent.

Effect of Tetrachloroethene

The effect of PCE was evaluated for soil PE samples containing weathered gasoline. Based on the liquid PE sample (neat material) analytical results, PCE was expected to have no effect on the TPH results for the PetroFLAG™ System; however, it was expected to bias the reference method results high.

Table 7-11 shows that PCE did not affect the PetroFLAG™ System TPH results for weathered gasoline soil PE samples, which confirmed the conclusions drawn from the results of the neat PCE analysis. However, when the PetroFLAG™ System result of greater than 20,000 mg/kg (an analytical outlier) was not considered, a Kruskal-Wallis one-way analysis of variance (nonparametric) and a Kruskal-Wallis pairwise comparison of means (nonparametric) showed that the mean TPH result without the interferent was the same as the mean TPH results with the interferent at the low and high levels and that the mean TPH result with the interferent at the low level was not the same as the mean TPH result with the interferent at the high level. When the analytical outlier was not considered, a simple comparison of mean TPH results showed that the mean TPH result was biased high at the low PCE level and that it was biased low at the high PCE level. Therefore, no conclusion was drawn regarding the effect of PCE on the TPH results for the PetroFLAG™ System.

For the reference method, at the interferent levels used, PCE was expected to bias the TPH results high by 24 percent (low level) and 113 percent (high level). The expected bias would be lower (20 and 92 percent, respectively) if PCE in soil samples was assumed to be extracted as efficiently as weathered gasoline in soil samples. The statistical tests showed that the probability of the three means being equal was less than 5 percent. However, the tests also showed that at the high level, PCE biased the TPH results high, which appeared to be reasonable based on the conclusions drawn from the analytical results for neat PCE. As to the reason for PCE at the low level having no effect on the TPH results, volatilization during PE sample preparation, transport, storage, and handling may have lowered the PCE concentrations to levels that would not have increased the TPH results beyond the reference method's precision (7 percent).

Effect of Stoddard Solvent

The effect of Stoddard solvent was evaluated for weathered gasoline and diesel soil PE samples. Based on the liquid PE sample (neat material) analytical results, Stoddard solvent was expected to bias both the PetroFLAG™ System and reference method results high. For the PetroFLAG™ System, at the interferent levels used, Stoddard solvent was expected to bias the TPH results high by 34 percent (low level) and 180 percent (high level) for weathered gasoline soil PE samples and by 52 percent (low level) and 260 percent (high level) for diesel soil PE samples. The expected bias would be higher (160 and 860 percent, respectively, for weathered gasoline soil PE samples) and lower (43 and 210 percent, respectively, for diesel soil PE samples) if Stoddard solvent in soil samples was assumed to be extracted as efficiently as weathered gasoline and diesel in soil samples. The statistical tests showed that the mean TPH results with and without the interferent were different for both weathered gasoline and diesel soil PE samples, which confirmed the conclusions drawn from the analytical results for neat Stoddard solvent.

For the reference method, at the interferent levels used, Stoddard solvent was expected to bias the TPH results high by 121 percent (low level) and 645 percent (high level) for weathered gasoline soil PE samples and by 114 percent (low level) and 569 percent (high level) for diesel soil PE samples. The expected bias would be lower (99 and 524 percent, respectively, for weathered gasoline soil PE samples and 61 and 289 percent, respectively, for diesel soil PE samples) if Stoddard solvent in soil samples was assumed to be extracted as efficiently as weathered gasoline and diesel in soil samples. The statistical tests showed that the mean TPH results with and without the interferent were different for both weathered gasoline and diesel soil PE samples, which confirmed the conclusions drawn from the analytical results for neat Stoddard solvent.

Effect of Turpentine

The effect of turpentine was evaluated for weathered gasoline and diesel soil PE samples. Based on the liquid PE sample (neat material) analytical results, turpentine was expected to bias both the PetroFLAG™ System and reference method results high.

For the PetroFLAG™ System, at the interferent levels used, turpentine was expected to bias the TPH results high by 78 percent (low level) and 370 percent (high level) for weathered gasoline soil PE samples and by 135 percent (low level) and 687 percent (high level) for diesel soil PE samples. The expected bias would be higher (380 and 1,770 percent, respectively, for weathered gasoline soil PE samples) and lower (110 and 560 percent, respectively, for diesel soil PE samples) if Stoddard solvent in soil samples was assumed to be extracted as efficiently as weathered gasoline and diesel in soil samples. The statistical tests showed that the mean TPH results with and without the interferent were different for both weathered gasoline and diesel soil PE samples, which confirmed the conclusions drawn from the analytical results for neat turpentine.

For weathered gasoline soil PE samples, when the PetroFLAG™ System result of greater than 100,000 mg/kg (an analytical outlier) was not considered, a Kruskal-Wallis one-way analysis of variance (nonparametric) and a Kruskal-Wallis pairwise comparison of means (nonparametric) were performed because the two remaining results could not be tested to determine whether they were normally distributed. The nonparametric tests showed that (1) the mean TPH result without the interferent and the mean TPH result with the interferent at the low level were equal and (2) the mean TPH results with the interferent at the low and high levels were equal, indicating that turpentine at the low level did not affect the TPH results for the weathered gasoline soil PE samples but that turpentine at the high level did affect the TPH results. The conclusion reached for the interferent at the low level was unexpected and did not seem reasonable based on a simple comparison of means that differed by a factor of three. The anomaly might have been associated with the nonparametric test used to evaluate the effect of turpentine on TPH results for weathered gasoline soil PE samples, as nonparametric tests do not account for the magnitude of the difference between TPH results.

For the reference method, at the interferent levels used, turpentine was expected to bias the TPH results high by 69 percent (low level) and 327 percent (high level) for weathered gasoline soil PE samples and by 72 percent (low level) and 371 percent (high level) for diesel soil PE samples. The expected bias would be lower (56 and 266 percent, respectively, for weathered gasoline soil PE samples and 39 and 200 percent, respectively, for diesel soil PE samples) if turpentine in soil samples was assumed to be extracted as efficiently as weathered gasoline and diesel in soil samples. The statistical tests showed that the mean TPH results with and without the interferent were different for weathered gasoline soil PE samples, which confirmed the conclusions drawn from the analytical results for neat turpentine. However, for diesel soil PE samples, (1) the mean TPH result without the interferent and the mean TPH result with the interferent at the low level were equal and (2) the mean TPH results with the interferent at the low and high levels were equal, indicating that turpentine at the low level did not affect the TPH results for the diesel soil PE samples but that turpentine at the high level did affect the TPH results. The conclusion reached for the interferent at the low level was unexpected and did not seem reasonable based on a simple comparison of means that differed by a factor of three. The anomaly might have been associated with the nonparametric test used to evaluate the effect of turpentine on TPH results for diesel soil PE samples, as nonparametric tests do not account for the magnitude of the difference between TPH results.

Effect of 1,2,4-Trichlorobenzene

The effect of 1,2,4-trichlorobenzene was evaluated for diesel soil PE samples. Based on the liquid PE sample (neat material) analytical results, 1,2,4-trichlorobenzene was expected to bias both the PetroFLAG™ System and reference method results high.

For the PetroFLAG™ System, at the interferent levels used, 1,2,4-trichlorobenzene was expected to bias the TPH results high by 18 percent (low level) and 90 percent (high level). The expected bias would be lower (15 and 74 percent, respectively) if 1,2,4-trichlorobenzene in soil samples was assumed to be extracted as efficiently as diesel in soil samples. The statistical tests showed that the mean TPH results with and without the interferent were different, which confirmed the conclusions drawn from the analytical results for neat 1,2,4-trichlorobenzene.

For the reference method, at the interferent levels used, 1,2,4-trichlorobenzene was expected to bias the TPH results high by 62 percent (low level) and 305 percent (high level). The expected bias would be lower (33 and 164 percent, respectively) if 1,2,4-trichlorobenzene in soil samples was assumed to be extracted as efficiently as diesel in soil samples. The statistical tests showed that the probability of three means being equal was less than 5 percent. However, the tests also showed that when the interferent was present at the high level, TPH results were biased high. The effect observed at the high level confirmed the conclusions drawn from the analytical

results for neat 1,2,4-trichlorobenzene. The statistical tests indicated that the mean TPH result with the interferent at the low level was not different from the mean TPH result without the interferent, indicating that the low level of 1,2,4-trichlorobenzene did not affect TPH measurement. However, a simple comparison of the mean TPH results revealed that the low level of 1,2,4-trichlorobenzene increased the TPH results to nearly the result based on the expected bias of 33 percent. Specifically, the mean TPH result with the interferent at the low level was 3,510 mg/kg rather than the expected value of 3,620 mg/kg. The conclusions drawn from the statistical tests were justified when the variabilities associated with the mean TPH results were taken into account.

Effect of Humic Acid

The effect of humic acid was evaluated for diesel soil PE samples. Based on the analytical results for soil PE samples containing humic acid, this interferent was expected to have no effect on the TPH results for the PetroFLAG™ System and reference method.

Table 7-11 shows that humic acid did not affect the PetroFLAG™ System TPH results for diesel soil PE samples, which confirmed the conclusions drawn from the analytical results for soil PE samples containing humic acid.

For the reference method, humic acid appeared to have biased the TPH results low. However, the bias decreased with an increase in the humic acid level. Specifically, the negative bias was 19 percent at the low level and 10 percent at the high level. For this reason, no conclusion was drawn regarding the effect of humic acid on TPH measurement using the reference method.

7.1.4 Primary Objective P4: Effect of Soil Moisture Content

To measure the effect of soil moisture content on the ability of the PetroFLAG™ System and reference method to accurately measure TPH, high-concentration-range soil PE samples containing weathered gasoline or diesel at two moisture levels were analyzed. The PetroFLAG™ System and reference method results were converted from a wet weight basis to a dry weight basis in order to evaluate the effect of moisture content on the sample TPH results. The PetroFLAG™ System and reference method dry weight TPH results were normally distributed; therefore, a two-tailed, two-sample Student's t-test was performed to determine whether the device and reference method results were impacted by soil moisture content—that is, to determine whether an increase in soil moisture content resulted in an increase or decrease in the TPH concentrations measured. The null hypothesis for the t-test was that the two means were equal or that the difference between the means was equal to zero. Table 7-12 shows the sample moisture levels, TPH results, mean TPH results for sets of triplicate samples, whether the mean TPH results at different moisture levels were the same, and the probability of the null hypothesis being true.

Table 7-12 shows that PetroFLAG™ System results for diesel soil samples at different moisture levels were statistically the same at a significance level of 5 percent but that this was not the case for weathered gasoline soil samples. Therefore, the PetroFLAG™ System results for weathered gasoline soil samples were impacted by soil moisture content. Based on a simple comparison of the results, this conclusion appeared to be reasonable.

Table 7-12 also shows that reference method results for weathered gasoline soil samples and diesel soil samples at different moisture levels were statistically the same at a significance level of 5 percent; therefore, the reference method results were not impacted by soil moisture content. Based on a simple comparison of the results, this conclusion appeared to be reasonable.

7.1.5 Primary Objective P5: Time Required for TPH Measurement

During the demonstration, the time required for TPH measurement activities, including PetroFLAG™ System setup, sample extraction and analysis and data package preparation, and PetroFLAG™ System disassembly, was measured. During the demonstration, two Dexsil field technicians performed the TPH measurement activities using the PetroFLAG™ System. Time measurement began at the start of each demonstration day when the technicians began to set up the PetroFLAG™ System and ended when they disassembled the device. Time not measured included (1) the time spent by the technicians verifying that they had received all the demonstration samples indicated on chain-of-custody forms and (2) the times when both technicians took breaks. In addition to the total time required for TPH measurement, the time required to perform sample extraction, perform sample analysis, and prepare the data package for the first and last analytical batches of soil samples was measured. The

Table 7-12. Comparison of Results for Soil Performance Evaluation Samples at Different Moisture Levels

Sample Type and Moisture Level	PetroFLAG™ System				Reference Method			
	TPH Result on Dry Weight Basis (milligram per kilogram)	Mean TPH Result (milligram per kilogram)	Were Mean TPH Results at Different Moisture Levels the Same or Different?[a]	Probability of Null Hypothesis Being True[b] (percent)	TPH Result on Dry Weight Basis (milligram per kilogram)	Mean TPH Result (milligram per kilogram)	Were Mean TPH Results at Different Moisture Levels the Same or Different?[a]	Probability of Null Hypothesis Being True[b] (percent)
Weathered gasoline at 9 percent moisture level	4,140	3,950	Different	2.36	2,070	2,230	Same	66.52
	4,020				2,220			
	3,700				2,400			
Weathered gasoline at 16 percent moisture level	3,040	3,270			2,070	2,300		
	3,520				2,390			
	3,260				2,440			
Diesel at less than 1 percent moisture level	3,340	3,300	Same	67.18	2,740	3,000	Same	71.95
	3,520				3,180			
	3,040				3,070			
Diesel at 9 percent moisture level	3,280	3,230			2,720	2,930		
	3,150				2,970			
	3,270				3,100			

Notes:

[a] A two-tailed, two-sample Student's t-test (parametric) was used to evaluate the effect of soil moisture content on TPH results.

[b] The null hypothesis for the t-test was that the two means were equal or that the difference between the two means was equal to zero.

number and type of samples in a batch were selected by Dexsil.

The time required to complete TPH measurement activities using the PetroFLAG™ System is shown in Table 7-13. When a given activity was performed by the two field technicians simultaneously, the time measurement for the activity was the total time spent by both technicians. The time required for each activity was rounded to the nearest 5 minutes.

Overall, Dexsil required 50 hours, 40 minutes, for TPH measurement of 66 soil environmental samples, 79 soil PE samples, 36 liquid PE samples, and 10 extract duplicates. Information regarding the time required for each measurement activity during the entire 3-day demonstration and for extraction, analysis, and data package preparation for the first and last batches of soil samples is provided below.

PetroFLAG™ System setup required 25 to 40 minutes each day, totaling 1 hour, 35 minutes, for the entire demonstration. This activity included PetroFLAG™ System setup; performing zero and standard calibrations of the PetroFLAG™ Analyzer; performing calibration checks of the digital balance; and organizing extraction, dilution, analysis, and waste disposal supplies. The setup time was measured on days 2 (25 minutes) and 3 (40 minutes) of the demonstration; therefore, the average setup time rounded to the nearest 5 minutes (30 minutes) was used to estimate the setup time for day 1 of the demonstration and the total setup time for the 3-day demonstration.

The sample extraction, sample analysis, and data package preparation times were not separately measured during the demonstration because these activities were performed concurrently by two field technicians. To report 191 TPH results, Dexsil performed 221 sample extractions, 39 dilutions, and 213 TPH analyses for soil samples and 45 dilutions and 50 TPH analyses for liquid PE samples. A total of 47 hours, 10 minutes, was required to perform these activities; therefore, an average of 10 minutes was required to perform these activities for one sample. The 263 TPH analyses included sample reanalyses as well as analyses of 10 extract duplicates. Throughout the demonstration, both technicians performed measurement activities.

The time required to perform extraction, analysis, and data package preparation for the first and last batches of soil samples was also recorded. A total of 2 hours, 20 minutes, was measured for the first batch of samples, which required 15 extractions, 11 dilutions, and 16 TPH analyses; therefore, an average of 9 minutes was required

Table 7-13. Time Required to Complete TPH Measurement Activities Using the PetroFLAG™ System

	Time Required[a]		
Measurement Activity	First Sample Batch[b]	Last Sample Batch[b]	3-Day Demonstration Period
PetroFLAG™ System setup	30 minutes[c]	40 minutes	1 hour, 35 minutes[c]
Sample extraction and analysis and data package preparation[d]	2 hours, 20 minutes	1 hour, 50 minutes	47 hours, 10 minutes
PetroFLAG™ System disassembly	40 minutes[e]	40 minutes	1 hour, 55 minutes[e]
Total	**3 hours, 30 minutes**	**3 hours, 10 minutes**	**50 hours, 40 minutes**

Notes:

[a] The time required for each activity was rounded to the nearest 5 minutes.

[b] The first sample batch required 15 soil sample extractions, 11 dilutions, and 16 TPH analyses. The last sample batch required 13 soil sample extractions and 13 sample extract TPH analyses.

[c] The setup time was measured on days 2 (25 minutes) and 3 (40 minutes) of the demonstration; therefore, the average setup time rounded to the nearest 5 minutes (30 minutes) was used to estimate the setup time for day 1 of the demonstration and the total setup time for the 3-day demonstration.

[d] The sample extraction, sample analysis, and data package preparation times were not separately measured during the demonstration because the field technicians performed these activities concurrently.

[e] The disassembly time was measured on days 2 (35 minutes) and 3 (40 minutes) of the demonstration; therefore, the average disassembly time rounded to the nearest 5 minutes (40 minutes) was used to estimate the disassembly time for day 1 of the demonstration and the total disassembly time for the 3-day demonstration.

to perform these activities for one sample. A total of 1 hour, 50 minutes, was measured for the last batch of samples, which required 13 extractions and 13 TPH analyses; therefore, an average of 8 minutes was required to perform these activities for one sample.

The decrease in the average analysis time between the first and last batches of soil samples appeared to be associated with the additional dilutions performed for the first batch of samples. The average analysis time for all the demonstration samples (10 minutes) exceeded the average analysis times for the first and last batches of samples and also appeared to be associated with the additional dilutions required throughout the demonstration.

PetroFLAG™ System disassembly required 35 to 40 minutes each day, totaling 1 hour, 55 minutes, for the entire demonstration. Disassembly included packing up the PetroFLAG™ System and associated supplies required for TPH measurement. The disassembly time was measured on days 2 (35 minutes) and 3 (40 minutes) of the demonstration; therefore, the average disassembly time rounded to the nearest 5 minutes (40 minutes) was used to estimate the disassembly time for day 1 of the demonstration and the total disassembly time for the 3-day demonstration.

During the weeks following the demonstration, Dexsil spent additional time revising the data package to address EPA comments. The revisions included correcting calculation and typographical errors for a few samples. The amount of additional time that Dexsil spent finalizing the data package could not be quantified and was not included as part of the time required for TPH measurement.

For the reference method, time measurement began when the reference laboratory received all the investigative samples and continued until the EPA received the first draft data package from the laboratory. The reference laboratory took 30 days to deliver the first draft data package to the EPA. Additional time taken by the reference laboratory to address EPA comments on all the draft laboratory data packages was not included as part of the time required for TPH measurement.

7.2 Secondary Objectives

This section discusses the performance results for the PetroFLAG™ System in terms of the secondary objectives stated in Section 4.1. The secondary objectives were addressed based on (1) observations of the PetroFLAG™ System's performance during the demonstration and (2) information provided by Dexsil.

7.2.1 Skill and Training Requirements for Proper Device Operation

Based on observations made during the demonstration, the PetroFLAG™ System is easy to operate, requiring one field technician with basic wet chemistry skills acquired on the job or in a university. For the demonstration, Dexsil chose to conduct sample analyses using two technicians in order to increase the sample throughput. One technician performed sample extractions while the other performed sample analyses.

The sample analysis procedure for the PetroFLAG™ System can be learned in the field with a few practice attempts. The device contains a user guide that must be followed to properly operate the device and a free training videotape and interactive compact disk. In addition, during regular business hours, Dexsil provides technical support over the telephone at no additional cost. Depending on the size of a project, Dexsil also provides on-site training upon request at no additional cost.

The carrying case of the PetroFLAG™ System contains a foam workstation that allows the user to keep enough items to perform 10 analyses organized and easily accessible. Also, items in the PetroFLAG™ Reagents kit and PetroFLAG™ High-Range Extraction Vials kit are organized in a configuration that resembles a test tube rack. Reagents in the PetroFLAG™ System are provided in premeasured, sealed vials. As a result, the likelihood of user error during sample analysis is minimized. The filter-syringe assembly provided as part of the device is small, lightweight, and designed such that little effort is required to filter sample extracts.

The PetroFLAG™ Analyzer allows a user in the field to select the response factor that is appropriate for the PHCs suspected to be present at a site. Table 2-1 lists the device's response factors, which range from 2 for weathered gasoline to 10 for transformer oil. Selection of an appropriate response factor is critical for obtaining accurate TPH results using the PetroFLAG™ System and may require significant user experience, especially when the sample contains a mixture of PHCs.

The response factor can be changed at any time without affecting the calibration data stored in the analyzer. The

microprocessor in the analyzer uses the calibration data and the response factor selected by the user to convert the optical reading into a TPH concentration in mg/kg. The user is not required to perform any calculations unless a soil to solvent mass ratio other than one is used to measure the TPH concentration or the sample extract is diluted. In such cases, the TPH concentration reported by the analyzer must be multiplied by the dilution factor used. After the demonstration, Dexsil made minimal revisions to the TPH results reported in the field. Specifically, of the 191 TPH results reported in the field at the end of the demonstration, fewer than 5 percent were corrected based on EPA review of the data package. The corrections primarily involved transcription errors.

To assist the user in obtaining accurate TPH measurements, the PetroFLAG™ Analyzer automatically performs several internal checks and informs the user when an error has occurred. For example, if a TPH concentration is outside the linear range of the analyzer but is still within the quantifiable range, the analyzer displays a blinking reading. If the TPH concentration is outside the quantifiable range of the analyzer, the analyzer displays a blinking "EEEE." According to Dexsil, acceptable precision for the linear and quantifiable ranges is ±10 percent and ±20 percent precision, respectively.

For cases in which a TPH concentration is outside the linear or quantifiable range of the PetroFLAG™ Analyzer, the user must select the most appropriate corrective action from among several options. According to the Dexsil user guide, the user may (1) decrease the soil to solvent mass ratio when the proprietary methanol mixture is used as the solvent or (2) use the high-range extraction solvent (proprietary glycol ether) to generate 1 mL of extract that is subsequently diluted in 10 mL of proprietary methanol mixture. Although it is not mentioned in the user guide, when the TPH concentration is outside the linear range but within the quantifiable range, the user may also dilute the sample extract produced using the proprietary methanol mixture and reanalyze the extract, thus eliminating the re-extraction step and reducing the amount of additional supplies required to perform the TPH measurement.

The PetroFLAG™ Analyzer is also equipped with a built-in temperature sensor that measures the ambient temperature during TPH measurement. The analyzer uses the sensor's temperature readings to correct for measurement fluctuations caused by temperature variations. However, the temperature corrections are valid only for ambient temperatures within 10 °C of the calibration temperature. Therefore, if the ambient temperature varies from the calibration temperature by more than 10 °C, an error condition results, and the analyzer has to be recalibrated.

The PetroFLAG™ Analyzer also automatically performs an optical system check. The analyzer has two independent optical channels. During TPH measurement, if the analyzer responses on the two channels are different, the analyzer displays an error message.

7.2.2 Health and Safety Concerns Associated with Device Operation

Sample analysis using the PetroFLAG™ System requires handling small quantities of a potentially hazardous proprietary methanol mixture (extraction solvent and zero calibration standard), proprietary glycol ether (high-concentration-range extraction solvent), and proprietary developer solution in sealed containers. Therefore, the user should employ good laboratory practices during sample analysis. Example guidelines for good laboratory practices are described in ASTM's "Standard Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water" (ASTM 1998).

During the demonstration, Dexsil field technicians operated the PetroFLAG™ System in modified Level D personal protective equipment (PPE) to prevent eye and skin contact with reagents. The PPE included safety glasses, disposable gloves, work boots, and work clothes with long pants. Sample analyses were performed outdoors in a well-ventilated area; therefore, exposure to the extraction solvents, zero calibration standard, and developer solution through inhalation was not a concern. Health and safety information for these reagents is included in material safety data sheets available from Dexsil. In addition, the user should exercise caution when handling the extraction and developer solution vials, which are made of glass.

7.2.3 Portability of the Device

The PetroFLAG™ System is easily transported between sampling areas in the field. Each PetroFLAG™ System starter kit weighs 11 pounds and is housed in a plastic carrying case that is 14 inches long, 19 inches wide, and 5.5 inches high. The PetroFLAG™ Analyzer alone weighs 0.6 pound and is 5.75 inches long, 3.5 inches wide, and 2 inches high. Each PetroFLAG™ Reagents kit, which contains enough supplies for 10 analyses, weighs

5 pounds and is housed in a cardboard box that is 13 inches long, 16 inches wide, and 9 inches high. Each PetroFLAG™ High-Range Extraction Vials kit, which contains enough supplies to perform 10 high-concentration-range extractions, weighs less than 3 pounds and is housed in a cardboard box that is 12 inches long, 8 inches wide, and 8 inches high. The Eppendorf™ 1-mL pipettor, which can be purchased separately from Dexsil, weighs less than 1 pound and is housed in a cardboard box that is 12 inches long, 8 inches wide, and 8 inches high. The PetroFLAG™ Analyzer, ACCULAB® digital balance, and digital timer are battery-operated. Because no AC power source is required, the system can be easily transported between sampling areas.

To operate the PetroFLAG™ System, a sample preparation and analysis area is required that is large enough to accommodate the items in one PetroFLAG™ System starter kit. A staging area may also be required to store PetroFLAG™ Reagents kits and PetroFLAG™ High-Range Extraction Vials kits; the size of the staging area depends on the number of samples to be analyzed and is thus project-specific. For the demonstration, Dexsil performed sample preparation and analysis under one 8- by 8-foot tent that housed two 8-foot-long, folding tables; three folding chairs; one 20-gallon laboratory pack for flammable waste; and one 55-gallon drum for general refuse.

7.2.4 Durability of the Device

The PetroFLAG™ System starter kit contains several reusable items, including the PetroFLAG™ Analyzer, ACCULAB® digital balance, and digital timer. An Eppendorf™ 1-mL pipettor, a reusable item, is used to perform high-concentration-range extractions. Based on observations made during the demonstration, the PetroFLAG™ System and the pipettor are durable; none of the reusable items malfunctioned or was damaged. The reusable items are manufactured or distributed by Dexsil or by scientific equipment suppliers and, except for the pipettor, are housed by Dexsil in a hard-plastic carrying case to prevent damage to the items during transport. The items were unaffected by the varying temperature and humidity conditions encountered between 8:00 a.m. and 5:00 p.m. on any given day of the demonstration. During the daytime, the temperature ranged from about 17 to 24 °C, while the relative humidity ranged from 53 to 88 percent. During sample analysis, the light, disposable items in the device were kept in the racks of the PetroFLAG™ Reagents kits, so wind speeds up to 20 miles per hour did not affect device operation.

7.2.5 Availability of the Device and Spare Parts

During the demonstration, neither the Eppendorf™ 1-mL pipettor nor any of the reusable items in the PetroFLAG™ System starter kit required replacement. Had any of these items required replacement, only a digital timer would have been available in local stores. A replacement item can be obtained from Dexsil by overnight courier service if the order is placed by 2:00 p.m. eastern time. If the need for a replacement item is identified after 2:00 p.m. eastern time and the item is needed the next day, each item may be obtained from various distributors of Dexsil products; the ACCULAB® digital balance and Eppendorf™ 1-mL pipettor may also be obtained from scientific equipment suppliers. Spare parts for reusable items such as the PetroFLAG™ Analyzer are not provided by Dexsil. Dexsil recommends that malfunctioning reusable items be returned to Dexsil for service; according to Dexsil, repairs should not be attempted in the field by the user. Because Dexsil provides a 6-month warranty for reusable items, Dexsil will replace such items and supply them to the user by overnight courier service at no additional cost during the warranty period.

The power supplies for the PetroFLAG™ Analyzer (one 9-volt battery), ACCULAB® digital balance (two CR2032 cell batteries), and digital timer (one G-13 button cell battery) can be purchased from local stores and replaced in the field if necessary.

Disposable items in the PetroFLAG™ System should be obtained from Dexsil or its authorized distributors. All the disposable items, including the breaktop vials containing proprietary methanol extraction solvent mixture, are manufactured only by Dexsil. The disposable items provided to a given user on a given occasion all come from the same lot. Because Dexsil conducts QC checks for each lot individually, if the user performs analyses with items from more than one lot or uses reagents obtained from a scientific supply store, Dexsil assumes no responsibility for the quality of the sample analysis results.

Chapter 8
Economic Analysis

As discussed throughout this ITVR, the PetroFLAG™ System was demonstrated by using it to analyze soil environmental samples, soil PE samples, and liquid PE samples. The environmental samples were collected from three contaminated sites, and the PE samples were obtained from a commercial provider, ERA. Collectively, the environmental and PE samples provided the different matrix types and the different levels and types of PHC contamination needed to perform a comprehensive economic analysis for the PetroFLAG™ System.

During the demonstration, the PetroFLAG™ System and the off-site laboratory reference method were each used to perform nearly 200 TPH analyses. The purpose of the economic analysis was to estimate the total cost of TPH measurement for the PetroFLAG™ System and then compare this cost to that for the reference method. The cost per analysis was not estimated for the PetroFLAG™ System because the cost per analysis would increase as the number of samples analyzed decreased. This increase would be primarily the result of the distribution of the initial capital equipment cost across a smaller number of samples. Thus, this increase in the cost per analysis cannot be fairly compared to the reference laboratory's fixed cost per analysis.

This chapter provides information on the issues and assumptions involved in the economic analysis (Section 8.1), discusses the costs associated with using the PetroFLAG™ System (Section 8.2), discusses the costs associated with using the reference method (Section 8.3), and presents a comparison of the economic analysis results for the PetroFLAG™ System and the reference method (Section 8.4).

8.1 Issues and Assumptions

Several factors affect TPH measurement costs. Wherever possible in this chapter, these factors are identified in such a way that decision-makers can independently complete a project-specific economic analysis. The following five cost categories were included in the economic analysis for the demonstration: capital equipment, supplies, support equipment, labor, and IDW disposal. The issues and assumptions associated with these categories and the costs not included in the analysis are briefly discussed below. Because the reference method costs were based on a fixed cost per analysis, the issues and assumptions discussed below apply only to the PetroFLAG™ System unless otherwise stated.

8.1.1 Capital Equipment Cost

The capital equipment cost was the cost associated with purchase of the PetroFLAG™ System starter kit used during the demonstration. The purchase price was obtained from a standard price list provided by Dexsil.

8.1.2 Cost of Supplies

The cost of supplies was estimated based on the supplies required to analyze all demonstration samples using the PetroFLAG™ System that were not included in the capital equipment cost category. Supplies used by Dexsil during the demonstration included (1) PetroFLAG™ Reagents kits, (2) PetroFLAG™ High-Range Extraction Vials kits, and (3) an Eppendorf™ 1-mL pipettor to accurately measure and transfer high-concentration-range sample extract into proprietary methanol solvent mixture. During

the demonstration, the quantity of supplies used by Dexsil were noted each day. The purchase price of these supplies was obtained from a standard price list provided by Dexsil. Because a user cannot return the unused supplies, no salvage value for supplies that were not used during the demonstration was included in the cost of supplies.

8.1.3 Support Equipment Cost

Because of the large number of samples analyzed during the demonstration, the EPA provided support equipment, including a tent, tables, and chairs, for the field technicians' comfort during sample extraction and analysis. For the economic analysis, the support equipment costs were estimated based on price quotes from independent sources.

8.1.4 Labor Cost

The labor cost was estimated based on the time required for PetroFLAG™ System setup, sample preparation, sample analysis, and summary data package preparation. The data package included, at a minimum, a result summary table, a run log, and any supplementary information submitted by Dexsil. The measurement of the time required for Dexsil to complete all analyses and submit the data package to the EPA was rounded to the nearest half-hour. However, for the economic analysis, it was assumed that a field technician who had worked for a fraction of a day would be paid for an entire 8-hour day. Based on this assumption, a daily rate for a field technician was used in the analysis.

During the demonstration, EPA representatives evaluated the skill level required for the field technicians to complete analyses and calculate TPH concentrations. Based on the field observations, a field technician with basic wet chemistry skills acquired on the job or in a university and a few hours of device-specific training was considered to be qualified to operate the PetroFLAG™ System. For the economic analysis, an hourly rate of $16.63 was used for a field technician (R.S. Means Company [Means] 2000), and a multiplication factor of 2.5 was applied to labor costs in order to account for overhead costs. Based on this hourly rate and multiplication factor, a daily rate of $332.60 was used for the economic analysis.

8.1.5 Investigation-Derived Waste Disposal Cost

During the demonstration, Dexsil was provided with two 20-gallon laboratory packs for collecting hazardous wastes generated (one for flammable wastes and one for corrosive wastes) and was charged for each laboratory pack used. Unused samples and sample extracts, residual solvent generated from sample extractions and dilutions, used EnCores, and unused chemicals that could not be returned to Dexsil were disposed of in a laboratory pack. Dexsil was required to provide any containers necessary to containerize individual wastes prior to their placement in a laboratory pack; however, Dexsil did not require additional containers. Items such as used PPE were disposed of with municipal garbage in accordance with demonstration site waste disposal guidelines; the associated waste disposal cost was not included in the IDW disposal cost estimate.

8.1.6 Costs Not Included

Items whose costs were not included in the economic analysis are identified below along with a rationale for the exclusion of each.

Oversight of Sample Analysis Activities. A typical user of the PetroFLAG™ System would not be required to pay for customer oversight of sample analysis. EPA representatives audited all activities associated with sample analysis during the demonstration, but costs for EPA oversight were not included in the economic analysis because these activities were project-specific. For the same reason, costs for EPA oversight of the reference laboratory were also not included in the analysis.

Travel and Per Diem for Field Technicians. Field technicians may be available locally. Because the availability of field technicians is primarily a function of the location of the project site, travel and per diem costs for field technicians were not included in the economic analysis.

Sample Collection and Management. Costs for sample collection and management activities, including sample homogenization and labeling, were not included in the economic analysis because these activities were project-specific and were not device- or reference method-dependent.

Shipping. Costs for shipping (1) the PetroFLAG™ System and necessary supplies to the demonstration site and (2) sample coolers to the reference laboratory were not included in the economic analysis because such costs vary depending on the shipping distance and the service used

(for example, a courier or overnight shipping versus economy shipping).

Items Costing Less Than $10. The cost of inexpensive items such as ice used for sample preservation in the field was not included in the economic analysis because the estimated cost was less than $10.

8.2 PetroFLAG™ System Costs

This section presents information on the individual costs of capital equipment, supplies, support equipment, labor, and IDW disposal for the PetroFLAG™ System as well as a summary of these costs. Additionally, Table 8-1 summarizes the PetroFLAG™ System costs.

8.2.1 Capital Equipment Cost

The capital equipment cost was the cost associated with the purchase of the PetroFLAG™ System starter kit (Item No. PETROFLAG™-MTR-01). Dexsil does not rent the PetroFLAG™ System starter kit. Table 2-2 lists the components of the kit, which contains the reusable equipment and disposable supplies required to perform 10 TPH measurements. Supplies required to perform additional measurements are sold separately. The PetroFLAG™ System starter kit can be purchased from Dexsil for $695.

Reusable items of the PetroFLAG™ System starter kit that can be purchased separately from Dexsil if additional quantities are needed include the PetroFLAG™ analyzer ($530), ACCULAB® digital balance ($132.50), and digital timer ($10.60). During the demonstration, no additional quantities of these items were required.

8.2.2 Cost of Supplies

Supplies used during the demonstration included the following: (1) PetroFLAG™ Reagents kits (Item No. PF-SRP); (2) an Eppendorf™ 1-mL pipettor (Item No. PC-1ML-PP), and (3) PetroFLAG™ High-Range Extraction Vials kits (Item No. PF-HRD). All supplies are available from Dexsil. The cost for the supplies are described below.

During the demonstration, Dexsil used 28 PetroFLAG™ Reagents kits. Table 2-2 lists the items included in a PetroFLAG™ Reagents kit. Each kit includes enough disposable supplies to perform 10 soil analyses. Because the price per kit decreases as the number of kits purchased increases, the purchase price per kit was $106. To perform high-concentration-range extractions, Dexsil used an Eppendorf™ 1-mL pipettor ($110) and four PetroFLAG™ High-Range Extraction Vials kits ($20 each). Each PetroFLAG™ High-Range Extraction Vials kit contains enough disposable extraction vials and replacement tips for

Table 8-1. PetroFLAG™ System Cost Summary

Item	Quantity	Unit Cost ($)	Itemized Cost[a] ($)
Capital equipment			
Purchase of PetroFLAG™ System starter kit	1 unit	695	695
Supplies			
PetroFLAG™ Reagents kit (supplies for 10 soil analyses)	28 units	106	2,968
PetroFLAG™ High-Range Extraction Vials kit (supplies for 10 high-concentration-range extractions)	4 units	20	80
Eppendorf™ 1-mL pipettor	1 unit	110	110
Support equipment			
Tent	1 unit	159	159
Tables and chairs (two each)	1 set for 1 week	39	39
Labor			
Field technicians	6 person-days	332.60	1,996
Investigation-derived waste disposal	1 20-gallon container	345	345
Total Cost[b]			**$6,390**

Notes:

[a] Itemized costs were rounded to the nearest $1.

[b] The total dollar amount was rounded to the nearest $10.

the pipettor to perform 10 high-range extractions. Thus, the total cost of supplies used by Dexsil during the demonstration was $3,158.

8.2.3 Support Equipment Cost

Dexsil was provided with one 8- by 8-foot tent for protection from inclement weather during the demonstration as well as two tables and two chairs for use during sample preparation and analysis activities. The purchase cost for the tent ($159) and the rental cost for two tables and two chairs for 1 week ($39) totaled $198.

8.2.4 Labor Cost

Two field technicians were required for 3 days each during the demonstration to complete all sample analyses and prepare the summary data package. Based on a daily labor rate of $332.60 per person, the total labor cost for the PetroFLAG™ System was $1,996 (rounded to the nearest $1).

8.2.5 Investigation-Derived Waste Disposal Cost

Dexsil used one laboratory pack to collect flammable hazardous waste generated during the demonstration. The IDW disposal cost included the purchase cost of the laboratory pack ($38) and the cost associated with hazardous waste disposal in a landfill ($307) (Means 2000). The total IDW disposal cost was $345.

8.2.6 Summary of PetroFLAG™ System Costs

The total cost for performing nearly 200 TPH analyses using the PetroFLAG™ System and for preparing a summary data package was $6,390 (rounded to the nearest $10). The TPH analyses were performed for 66 soil environmental samples, 79 soil PE samples, and 36 liquid PE samples. In addition to these 181 samples, 10 extract duplicates were analyzed for specified soil environmental samples. When Dexsil performed multiple extractions, dilutions, reanalyses, or field duplicates for a sample, these were not included in the number of samples analyzed. During the demonstration, the multiple extractions, dilutions, reanalyses, and field duplicates collectively required 9 additional PetroFLAG™ Reagents kits (about 47 percent more).

The total cost of $6,390 for analyzing the demonstration samples using the PetroFLAG™ System included $695 for capital equipment; $3,158 for supplies; $198 for support equipment; $1,996 for labor; and $345 for IDW disposal. Of these five costs, the two largest were the cost of supplies (49 percent of the total cost) and the labor cost (31 percent of the total cost).

8.3 Reference Method Costs

This section presents the costs associated with the reference method used to analyze the demonstration samples for TPH. Depending on the nature of a given sample, the reference laboratory analyzed the sample for GRO, EDRO, or both and calculated the TPH concentration by adding the GRO and EDRO concentrations, as appropriate. The reference method costs were calculated using unit cost information from the reference laboratory invoices. To allow an accurate comparison of the PetroFLAG™ System and reference method costs, the reference method costs were estimated for the same number of samples as was analyzed by Dexsil. For example, although the reference laboratory analyzed MS/MSD samples for TPH and all soil samples for percent moisture, the associated sample analytical costs were not included in the reference method costs because Dexsil did not analyze MS/MSD samples for TPH or soil samples for percent moisture during the demonstration.

Table 8-2 summarizes the reference method costs, which totaled $38,560. This cost covered preparation of demonstration samples and their analysis for TPH. In addition, at no additional cost, the reference laboratory provided (1) analytical results for internal QC check samples such as method blanks and LCS/LCSDs and (2) an electronic data deliverable and two paper copies of full, EPA Contract Laboratory Program-style data packages within 30 calendar days of the receipt of the last demonstration sample by the reference laboratory.

8.4 Comparison of Economic Analysis Results

The total costs for the PetroFLAG™ System ($6,390) and the reference method ($38,560) are listed in Tables 8-1 and 8-2, respectively. The total TPH measurement cost for the PetroFLAG™ System was 83 percent less than that for the reference method. Although the PetroFLAG™ System did not provide the same level of detail (for example, carbon ranges) as the reference method analytical results or comparable QA/QC data, the PetroFLAG™ System provided TPH analytical results on site at significant cost savings. In addition, use of the PetroFLAG™ System in

Table 8-2. Reference Method Cost Summary

Item	Number of Samples Analyzed	Cost per Analysis ($)	Itemized Cost[a] ($)
Soil environmental samples			
GRO	56	111	6,216
Extract duplicates	9	55.50	500
EDRO	66	142	9,372
Extract duplicates	10	71	710
Soil performance evaluation samples			
GRO	45	111	4,995
EDRO	79	142	11,218
Liquid performance evaluation samples			
GRO	27	111	2,997
EDRO	24	106.50	2,556
Total Cost[b]			**$38,560**

Notes:

[a] Itemized costs were rounded to the nearest $1.

[b] The total dollar amount was rounded to the nearest $10.

the field will likely produce additional cost savings because the results will be available within a few hours of sample collection; therefore, critical decisions regarding sampling and analysis can be made in the field, resulting in a more complete data set. However, these savings cannot be accurately estimated and thus were not included in the economic analysis.

Chapter 9
Summary of Demonstration Results

As discussed throughout this ITVR, the PetroFLAG™ System was demonstrated by using it to analyze 66 soil environmental samples, 79 soil PE samples, and 36 liquid PE samples. In addition to these 181 samples, 10 extract duplicates prepared using the environmental samples were analyzed. The environmental samples were collected from four individual areas at three contaminated sites, and the PE samples were obtained from a commercial provider, ERA. Collectively, the environmental and PE samples provided the different matrix types and the different levels and types of PHC contamination needed to perform a comprehensive evaluation of the PetroFLAG™ System.

The PetroFLAG™ System performance and cost data were compared to those for an off-site laboratory reference method, SW-846 8015B (modified). As discussed in Chapter 6, the reference method results were considered to be of adequate quality for the following reasons: (1) the reference method was implemented with acceptable accuracy (± 30 percent) for all the samples except low- and medium-concentration-range soil samples containing diesel, which made up only 13 percent of the total number of samples analyzed during the demonstration, and (2) the reference method was implemented with good precision for all samples. The reference method results generally exhibited a negative bias. However, the bias was considered to be significant primarily for low- and medium-range soil samples containing diesel. The reference method recoveries observed during the demonstration were typical of the recoveries obtained by most organic analytical methods for environmental samples.

This chapter compares the performance and cost results for the PetroFLAG™ System with those for the reference method, as appropriate. The performance and cost results are discussed in detail in Chapters 7 and 8, respectively. Tables 9-1 and 9-2 summarize the results for the primary and secondary objectives, respectively. As shown in these tables, during the demonstration, the PetroFLAG™ System exhibited the following desirable characteristics of a field TPH measurement device: (1) good precision, (2) lack of sensitivity to interferents that are not petroleum hydrocarbons (PCE and humic acid), (3) low measurement costs, and (4) ease of use. In addition, the PetroFLAG™ System exhibited moderate sample throughput.

Based on action level conclusions and statistical correlations, the PetroFLAG™ System TPH results compared well with those of the reference method; however, the device exhibited a high bias, and its TPH results were determined to be statistically different from those of the reference method. In addition, turpentine and 1,2,4-trichlorobenzene biased the PetroFLAG™ System TPH results high; the reference method TPH results were also biased high by turpentine and 1,2,4-trichlorobenzene, but the extent of the impact on the reference method was significantly less. These findings indicated that the accuracy of TPH measurement using the device may be significantly impacted by naturally occurring oil and grease and chlorinated semivolatile organic contaminants such as chlorinated pesticides and PCBs present in soil samples. Also, the device exhibited sensitivity to soil moisture content during TPH measurement of weathered gasoline soil samples but not diesel soil samples. Specifically, the TPH results for weathered gasoline soil samples were biased low (17 percent) when the soil moisture content was increased from 9 to 16 percent. Collectively, the demonstration findings indicated that the user should exercise caution when considering the device for a specific field TPH measurement application.

Table 9-1. Summary of PetroFLAG™ System Results for the Primary Objectives

Primary Objective	Evaluation Basis[a]	Performance Results	
		PetroFLAG™ System	Reference Method
P1 Determine the method detection limit	Method detection limit based on TPH analysis of seven low-concentration-range diesel soil PE samples	20 mg/kg	6.32 mg/kg
P2 Evaluate the accuracy and precision of TPH measurement	Comparison of project-specific action level conclusions of the PetroFLAG™ System with those of the reference method for 66 soil environmental and 31 soil PE samples	71 of 97 PetroFLAG™ System conclusions (73 percent) agreed with those of the reference method; 26 PetroFLAG™ System conclusions were false positives.	
	Comparison of PetroFLAG™ System TPH results with those of the reference method for 66 soil environmental and 25 soil PE samples	11 of 91 PetroFLAG™ System results (12 percent) were within 30 percent of the reference method results; 7 PetroFLAG™ System results were biased high, and 4 were biased low. 9 of 91 PetroFLAG™ System results (10 percent) were within 30 to 50 percent of the reference method results; 8 PetroFLAG™ System results were biased high, and 1 was biased low. 71 of 91 PetroFLAG™ System results (78 percent) were not within 50 percent of the reference method results; 67 PetroFLAG™ System results were biased high, and 4 were biased low.	
	Pairwise comparison of PetroFLAG™ System and reference method TPH results for (1) soil environmental samples collected from four areas; (2) soil PE samples, including blank, weathered gasoline, and diesel soil samples; and (3) liquid PE samples consisting of neat weathered gasoline and diesel	For soil environmental samples, the PetroFLAG™ System results were statistically (1) the same as the reference method results for one of the four sampling areas and (2) different from the reference method results for three of the sampling areas. For soil PE samples, the PetroFLAG™ System results were statistically (1) the same as the reference method results for high-concentration-range diesel samples and (2) different from the reference method results for blank samples, high-concentration-range weathered gasoline samples, and low- and medium-concentration-range diesel samples. For liquid PE samples, the PetroFLAG™ System results were statistically different from the reference method results for both weathered gasoline and diesel samples.	
	Correlation (as determined by linear regression analysis) between PetroFLAG™ System and reference method TPH results for (1) soil environmental samples collected from four areas and (2) soil PE samples, including weathered gasoline and diesel soil samples	The PetroFLAG™ System results correlated highly with the reference method results for one of the four sampling areas and diesel soil PE samples (R^2 values were greater than 0.90, and F-test probability values were less than 5 percent). The PetroFLAG™ System results correlated moderately with the reference method results for two of the four sampling areas (R^2 values were 0.84 and 0.86, and F-test probability values were less than 5 percent). The PetroFLAG™ System results correlated weakly with the reference method results for one of the four sampling areas and weathered gasoline soil PE samples (R^2 values were 0.42 and 0.10, respectively, and F-test probability values were greater than 5 percent).	

Table 9-1. Summary of PetroFLAG™ System Results for the Primary Objectives (Continued)

Primary Objective	Evaluation Basis[a]	Performance Results	
		PetroFLAG™ System	Reference Method
P2 Evaluate the accuracy and precision of TPH measurement (continued)	Overall precision (RSD) for soil environmental, soil PE, and liquid PE sample replicates	Soil environmental samples (11 triplicates) RSD range: 7 to 38 percent Median RSD: 19 percent	Soil environmental samples (11 triplicates) RSD range: 4 to 39 percent Median RSD: 16 percent
		Soil PE samples (7 replicates) RSD range: 2 to 9 percent Median RSD: 6 percent	Soil PE samples (6 replicates) RSD range: 6 to 13 percent Median RSD: 8 percent
		Liquid PE samples (2 triplicates) RSDs: 3 and 9 percent Median RSD: 6 percent	Liquid PE samples (2 triplicates) RSDs: 5 and 6 percent Median RSD: 5.5 percent
	Analytical precision (RPD) for extract duplicates for soil environmental samples (10 for the PetroFLAG™ System and 12 for the reference method)	RPD range: 1 to 26 Median RPD: 5	RPD range: 0 to 11 Median RPD: 4
P3 Evaluate the effect of interferents on TPH measurement	Mean responses for neat materials, including MTBE; PCE; Stoddard solvent; turpentine; and 1,2,4-trichlorobenzene, and for soil spiked with humic acid (two triplicate sets each)	MTBE: 0 percent PCE: 1.5 percent Stoddard solvent: 42.5 percent Turpentine: 103 percent 1,2,4-Trichlorobenzene: 16 percent Humic acid: 2.5 percent	MTBE: 39 percent PCE: 17.5 percent Stoddard solvent: 85 percent Turpentine: 52 percent 1,2,4-Trichlorobenzene: 50 percent Humic acid: 0 percent
	Comparison of TPH results (one-way analysis of variance) for weathered gasoline and diesel soil PE samples without and with interferents at two levels Interferents for weathered gasoline soil PE samples: MTBE, PCE, Stoddard solvent, and turpentine Interferents for diesel soil PE samples: Stoddard solvent; turpentine; 1,2,4-trichlorobenzene; and humic acid	MTBE, a petroleum hydrocarbon, caused statistically significant interference only at the high level.	MTBE, a petroleum hydrocarbon, did not cause statistically significant interference at either of the two levels.
		PCE results were inconclusive.	PCE caused statistically significant interference only at the high level.
		Stoddard solvent, a petroleum hydrocarbon, caused statistically significant interference at both levels for weathered gasoline and diesel samples.	Stoddard solvent, a petroleum hydrocarbon, caused statistically significant interference at both levels for weathered gasoline and diesel samples.
		Turpentine caused statistically significant interference at both levels for weathered gasoline and diesel samples.	Turpentine caused statistically significant interference (1) at both levels for weathered gasoline samples and (2) only at the high level for diesel samples.
		1,2,4-Trichlorobenzene caused statistically significant interference at both levels.	1,2,4-Trichlorobenzene caused statistically significant interference only at the high level.
		Humic acid did not cause statistically significant interference at either of the two levels.	Humic acid results were inconclusive.
P4 Evaluate the effect of soil moisture content on TPH measurement	Comparison of TPH results (two-sample Student's t-test) for weathered gasoline and diesel soil PE samples at two moisture levels: 9 and 16 percent for weathered gasoline samples and less than 1 and 9 percent for diesel samples	Soil moisture content had a statistically significant impact on weathered gasoline sample results.	Soil moisture content did not have a statistically significant impact.

Table 9-1. Summary of PetroFLAG™ System Results for the Primary Objectives (Continued)

Primary Objective	Evaluation Basis[a]	Performance Results	
		PetroFLAG™ System	Reference Method
P5 Measure the time required for TPH measurement (sample throughput)	Total time from sample receipt through preparation of the draft data package	50 hours, 40 minutes, for TPH measurement of 66 soil environmental samples, 79 soil PE samples, 36 liquid PE samples, and 10 extract duplicates	30 days for TPH measurement of 74 soil environmental samples, 89 soil PE samples, 36 liquid PE samples, and 13 extract duplicates
P6 Estimate TPH measurement costs	Total cost (costs of capital equipment, supplies, support equipment, labor, and IDW disposal) for TPH measurement of 66 soil environmental samples, 79 soil PE samples, 36 liquid PE samples, and 10 extract duplicates	$6,390 (including the capital equipment purchase cost of $695 for the PetroFLAG™ System starter kit)	$38,560

Notes:

IDW = Investigation-derived waste
mg/kg = Milligram per kilogram
MTBE = Methyl-tert-butyl ether
PCE = Tetrachloroethene
PE = Performance evaluation
R^2 = Square of the correlation coefficient
RPD = Relative percent difference
RSD = Relative standard deviation

[a] All statistical comparisons were made at a significance level of 5 percent.

Table 9-2. Summary of PetroFLAG™ System Results for the Secondary Objectives

Secondary Objective	*Performance Results*
S1 Skill and training requirements for proper device operation	The device can be operated by one person with basic wet chemistry skills. The device's user guide, training videotape, and interactive compact disk are considered to be adequate training materials for proper device operation. The sample analysis procedure for the device can be learned in the field with a few practice attempts. The device's digital display provides a sample's TPH concentration in milligrams per kilogram on a wet weight basis; minimal effort is required to calculate a TPH concentration when a soil to solvent mass ratio other than one is used or when sample extract dilution is involved. At the end of the demonstration, Dexsil reported 191 TPH results. Of these, fewer than 5 percent required corrections, which primarily involved transcription errors.
S2 Health and safety concerns associated with device operation	No significant health and safety concerns were noted; when the device is used in a well-ventilated area, basic eye and skin protection (safety glasses, disposable gloves, work boots, and work clothes with long pants) should be adequate for safe device operation.
S3 Portability of the device	The device is battery-operated and requires no alternating current power source. The device can be easily moved between sampling areas in the field, if necessary.
S4 Durability of the device	The device is provided in a hard-plastic carrying case to prevent damage to the device. During the demonstration, none of the device's reusable items malfunctioned or was damaged. The moderate temperatures (17 to 24 °C) and high relative humidities (53 to 88 percent) encountered during the demonstration did not affect device operation.
S5 Availability of device and spare parts	All items in the device are available from Dexsil. During a 6-month warranty period, Dexsil will supply replacement parts for the device by overnight courier service at no cost unless the reason for a part failure involves misuse of the device.

Chapter 10
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Appendix
Supplemental Information Provided by the Developer

This appendix contains supplemental information provided by Dexsil. After the introduction, this appendix discusses the PetroFLAG™ System, the effect of naturally occurring organic compounds on TPH measurement using the device, and the importance of the choice of the response factor.

Introduction

Dexsil would like to thank the EPA for undertaking the demonstration project. As a developer of field test kit technologies, Dexsil believes that programs like the SITE Program are a valuable contribution to environmental efforts everywhere and that the EPA, as a government agency, is the only organization with the credentials to conduct these types of unbiased evaluations. Dexsil also believes that the subject of TPH measurement of soil is especially important because of the unique complexities associated with both definition of TPH as an analyte and comparison of dissimilar laboratory or field analytical methods. Dexsil would also like to thank Tetra Tech EM Inc. for doing such a great job in organizing and running the field demonstration and coordinating all the logistical aspects of the project.

As a result of the predemonstration phase of the study and subsequent discussions with developers, contractors, and the EPA, there were a number of issues associated with measurement of TPH in soil that had to be resolved. Because TPH itself is defined by the method used to measure it, the choice of a reference method and verification of the method's performance were the two major concerns of the developers. Although the study was not intended to be an evaluation and verification of laboratory methods, Dexsil would like to thank the EPA for taking the first step in developing and validating laboratory analytical methods for TPH in soil. The results obtained in this study should provide a good starting point for further work on method validation. The discussions in the previous sections of this ITVR illustrate the difficulties associated with independent validation of a reference method.

The following discussion has been contributed in the interest of presenting an evaluation of some of the aspects of the demonstration that are of particular importance to PetroFLAG™ System users. The preliminary statistical analyses presented were performed as references for the discussion and are not intended to replace the analysis presented in the previous sections of this ITVR. Dexsil made every effort to follow standard statistical methods. There might be small differences in the specific results obtained by the EPA and Dexsil, but the overall conclusions drawn below should still be valid. It is hoped that this information will help field technicians develop a more complete understanding of the use of the PetroFLAG™ System as well as other field technologies in light of the difficulties associated with TPH measurement of soil.

The PetroFLAG™ System

The PetroFLAG™ System used during the SITE demonstration was the standard production analyzer sold by Dexsil. This analyzer has been in use in the field since 1995. All the reagents used were standard reagents, and

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the analytical procedures used were the standard procedures described in the device's user manual and in SW-846 Method 9074.

Designed in the early 1990s to overcome environmental and technical problems associated with the then current methods for measurement of TPH in soil, the PetroFLAG™ System uses no chlorofluorocarbons, is generally not affected by soil moisture content below 15 percent, and is fully field-portable. The key to the versatility of the PetroFLAG™ System is the patented solvent/developer solution system. The water-miscible solvent is designed to extract all nonpolar hydrocarbons across a broad range of molecular weights and classes. The extracted hydrocarbons are then precipitated by the developer solution to form a turbid aqueous suspension.

The PetroFLAG™ System provides a predictable and reproducible response for a broad range of hydrocarbon mixtures found in the environment. Because the PetroFLAG™ System responds to hydrocarbons based on their nonpolar nature and not on a particular functional group or fluorescence spectrum, the accuracy of a final TPH result is a predicable function of the "mean molecular weight" of the contaminant hydrocarbon. Depending on the makeup of the hydrocarbon, the response of the PetroFLAG™ System can be adjusted to the specific contaminant present using a response factor determined at the factory or in the field. Because the response factors are simply multiplicative constants applied to the raw PetroFLAG™ System readings, the results obtained in the field can be corrected as confirmatory laboratory results become available.

The Effect of Naturally Occurring Organic Compounds

With the PetroFLAG™ System, any naturally occurring, nonpolar, hydrocarbon-like compounds may be quantified as TPH. For this reason, naturally occurring hydrocarbons tend to elevate the device's TPH results. This can occur if surface soils are included in a sample or if a project site has had a history of industrial activity during which soil layers may have been mixed during excavation activities. If naturally occurring hydrocarbons are present at a site, an estimate of the background concentration can be obtained by using both device and laboratory results for samples collected either on site or off site. Provided that the laboratory is reliable, either option is acceptable. The former option requires more samples to arrive at a statistically valid background concentration estimate; the latter option can be implemented using fewer samples but requires that the "blank" samples be truly free of hydrocarbon contamination.

For the NEX Service Station Area samples, both during the predemonstration investigation and the demonstration, the regression analyses indicate that background organics were present at concentrations between 400 and 600 mg/kg. Despite the presence of nonhydrocarbon organics and the associated increased variability in the NEX Service Station Area samples, the correlation of the PetroFLAG™ System results with the laboratory results was still reasonable. Because naturally occurring organic compounds are generally not uniformly distributed throughout soil strata and because they are not included in the definition of TPH, if they are present, they tend to add variability to the sample TPH results. Although the regression analysis of the data for the other sampling areas resulted in a positive intercept, the intercepts were not statistically significant, indicating that significant background concentrations were not present. It should be noted that ERA made the PE samples from processed garden soil, which has approximately 100 to 200 mg/kg of organic background material as measured by the PetroFLAG™ System. Both the predemonstration investigation sample results and the demonstration soil PE sample results showed this background concentration.

The Importance of the Choice of the Response Factor

As is the case with all the field devices evaluated in the study, the PetroFLAG™ System does not measure all the individual compounds that are quantified as TPH by a laboratory method using GC analysis. The PetroFLAG™ System measures a specific property of hydrocarbons and, using a conversion algorithm, converts this measurement into an equivalent TPH value. In the case of the PetroFLAG™ System, the conversion algorithm is simply an empirically determined multiplier applied to the turbidity reading for the final solution. Because the

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conversion multiplier, or response factor, is roughly proportional to the mean molecular weight or carbon number of the PHCs, simply knowing which petroleum product is present allows predetermined response factors to be used for all soil samples from a site. Determining the correct response factor for unknown or mixed contaminants requires some preliminary analysis, but once the contamination has been characterized, the appropriate response factor can be selected, and any results already obtained can be corrected using this response factor.

Accurate laboratory characterization of the hydrocarbon present is crucial to the conversion of field readings into meaningful TPH results. Not only is it important to choose the correct analytical method, but the laboratory must also be proficient in using the chosen method. Because the PetroFLAG™ System is designed to measure TPH, it is important that a TPH method be specified as the reference method. Using a specific petroleum method, such as a GRO, DRO, EPH, or VPH method, may result in underestimation of the TPH concentration. Similarly, using a laboratory that has not demonstrated proficiency in using TPH methods will lead to inaccurate results. Dexsil recommends that any prospective laboratory be thoroughly evaluated before it is used and that its performance be monitored. This evaluation should involve laboratory analysis of soils spiked with the appropriate hydrocarbons, duplicate field samples, and samples that are both wet and dry.

The sample set used in the study provided a good illustration of the different factors that must be considered in choosing the correct response factor. Dexsil recommends (and in some cases, it is required) that confirmatory split samples be sent to a qualified laboratory as part of a remediation project. The response factor chosen must always be a balance between the correct response factor for the contaminant present and the response factor that will match the laboratory results.

The choice of the correct response factors for the study was somewhat complicated by the predemonstration investigation results. On one hand, the reference method indicated that the PetroFLAG™ System was overestimating TPH concentrations. On the other hand, Dexsil's laboratory analysis of the predemonstration investigation samples indicated that the device obtained correct results using the predetermined response factors for the hydrocarbon mixtures present. To resolve this conflict, Dexsil looked at the results of the PE sample analyses. The EDRO PE sample results indicated that the reference method results were biased low: the recoveries were 54 and 64 percent for the two samples analyzed. For these two samples, the Dexsil laboratory recoveries were 97 and 112 percent, respectively; and the PetroFLAG™ System recoveries (without a dilution effect correction) were 97 and 103 percent, respectively. The ratio of the average recoveries predicted the slope of the regression line for the comparison of the PetroFLAG™ System and reference laboratory results. This information, combined with 5 years of historical data, indicated that Dexsil's choice of response factors based on the predetermined values for each of the sampling areas would provide accurate results.

The drawback in choosing conservative response factors as described above was that the PetroFLAG™ System results might be high relative to the reference method results if the reference method results were biased low. The choice of response factors was conservative because, from a remediation point of view, a false positive is preferable to a false negative. Choosing a response factor that underreported the results to match the reference method recoveries would have resulted in underestimation of the true TPH concentration, and if the reference method recoveries improved for some soil types, the PetroFLAG™ System results would then be biased low relative to the reference method results. As discussed in Chapter 7, this is indeed what happened. An analysis of the data for both the FFA and SFT Area samples (primarily silty clay) indicated that the PetroFLAG™ System results were biased high relative to the reference method results. In comparison, the device results from the NEX Service Station Area samples (primarily sand) showed no significant bias relative to the reference method results. Insufficient data were available to perform a regression analysis of the B-38 Area sample data. Most of the data for the B-38 Area samples were at or below the method quantitation limit for the PetroFLAG™ System.

The results for the PE samples confirmed the low bias of the reference method results. The reference method's diesel sample recoveries were 55, 70, and 67 percent, and

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its gasoline sample recoveries were 61 and 62 percent. The PetroFLAG™ System recoveries were 114, 75, and 75 percent for the diesel samples and 115 and 98 percent for the gasoline samples, respectively. Recoveries for the hydrocarbon-like compounds such as Stoddard solvent and turpentine were also lower for the reference method than for the PetroFLAG™ System (see Chapters 6 and 7). Although analysis of PE samples does not provide a direct indication of the performance of a particular method for field samples, PE sample analysis provides the only independent test of the "accuracy" of either a laboratory or field method. The recoveries obtained for PE samples could be considerably worse or better than those obtained for field samples. For the demonstration, the PE samples were made from relatively uniform, easily extractable soil. Field samples may not be so easy to extract.

In a situation where the reference method used by regulators is biased high or low, the PetroFLAG™ System response factor can be adjusted to provide data that matches the reference method data. For example, using a response factor of 10 instead of 6 for the FFA samples brings the PetroFLAG™ System data into agreement with the reference method data. For the SFT Area samples, using a response factor of 4 instead of 2 brings the device results into better agreement with the reference method results. Changing the response factor does not, however, change the correlation, which was very good for these two sample sets. The device data for the NEX Service Station Area samples (primarily sandy soil) agreed with the reference method data and would not be recalculated.

The above discussions are in no way exhaustive, but they should provide some guidance for interpretation of the data generated during the study. Overall, the PetroFLAG™ System performed as expected, exhibiting good correlation with the reference method, reasonable recoveries for the PE samples, and predictable results for the liquid PE samples.

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