



Brown & Root Environmental

N62661.AR 000895
NAVSTA NEWPORT RI
5090.3a
55 Jonspin Road
Wilmington, MA 01887-1062

Phone: (508) 658-7899
FAX (508) 658-7870

C-NAVY-6-97-0195W

June 26, 1997

Project Number 7578

Mr. Paul Kulpa, Project Manager
Department of Environmental Management
Division of Site Remediation
291 Promenade Street
Providence, Rhode Island 02908-5767

Reference: Contract No. N62472-90-D-1298
Contract Task Order (CTO) No. 0288

Subject: Response to EPA Review Comments for Work Plan for Source Removal Evaluation
Old Fire Fighting Training Area, NETC, Newport, Rhode Island

Dear Mr. Kulpa,

Enclosed are responses to the RIDEM's review comments for the Work Plan to perform a limited source removal evaluation. Brown & Root (B&R) Environmental prepared these comments on behalf of the U.S Navy Please note the following key modifications based on the review comments:

- Three borings/monitoring wells would be included in the field program to supplement the existing well network.
- Analyses of shoreline sediment samples for PCBs and TPH have been included.
- Sample summary tables have been revised to reflect these changes and other typographic corrections.
- Total petroleum hydrocarbons will be analyzed by EPA Method 8100 (modified), based on discussions with an analytical laboratory and a member of the RIDEM UST program.

If you should have any questions, please do not hesitate to contact me at (508) 658-7899.

Yours truly,

Liyang Chu
Project Manager

LC/rt

Enclosures

c: J. Shafer/T. Bober - NORTHDIV (w/enc)
K. Keckler - USEPA (w/enc)
B. Wheeler - NETC (w/enc.)
J Trepanowski/M. Turco - B&R Environmental (w/enc.)
File 7578 - 3.2 (w/enc.)

RESPONSE TO RIDEM COMMENTS
WORK PLAN FOR LIMITED SOURCE REMOVAL EVALUATION
Old Fire Fighting Training Area, NETC - Newport, RI
CTO 0288
June 26, 1997

Response to General Comment 1 RE: Obtaining information from NETC employees.

Former NETC employees (i.e. firefighters), if available, will be interviewed by NETC Environmental personnel prior to commencement of field activities to help identify the target subsurface features. Mr. Paul Kulpa, RIDEM, stated that he has spoken with one former firefighter. If the name of that person could be provided to Navy, this would help in Navy's efforts.

Response to General Comment 2 RE: Record search for site specific plans.

An extensive record search of archived records and drawings was performed by NETC personnel Brown & Root Environmental (B&RE) in October 1996. Because of the limitations of some of the drawings/plans (i.e. design drawings vs. as-builts), as recognized in the work plan and as requested by RIDEM, another attempt has been made to obtain site-specific plans prior to commencement of field operations. NETC personnel reviewed the listing of available engineering drawings and found a few additional drawings that may be of use to refining the selection of test pit locations. The current investigation goal is to confirm the presence or absence of subsurface features, such as USTs and piping, that could be potential sources of petroleum products or other chemicals.

Given the limited time frame available to conduct the field investigations at Site 09, it would not be possible at this time for the Navy to obtain information from other similar training facilities at other bases. As discussed during the conference call of June 5, NORTHDIV personnel in Lester, Pennsylvania have initiated inquiries into such records for future uses during the remaining portions of the Remedial Investigation.

Response to General Comment 3 RE: Removal Work Plan and various activities to be initiated during the source evaluation.

Should a removal action be warranted, the Navy will develop and submit an appropriate work plan to RIDEM, taking into consideration their recommendations and/or procedures for the removal of contaminated soils.

Response to General Comment 3 RE: Analytical methods

During the proposed limited source removal evaluation, initial screening of the soils will entail visual observations coupled with jar headspace FID instrument readings to select samples for laboratory analysis. As discussed with RIDEM on June 5, additional research has been conducted to identify monitoring instruments that would be used to evaluate for potential petroleum hydrocarbon presence. Specifically, B&RE will use a FID instrument to monitor for volatile organic compounds and low molecular weight semi-volatile organic compounds (SVOCs) in lieu of attempting to detect petroleum compounds using olfactory means (which pose health and safety issues).

If a removal action is warranted and implemented, field monitoring instruments and one additional field screening analysis (i.e. field IR, field GC, immunoassay, or UV absorbance) will likely be utilized to select confirmatory samples for laboratory analysis. Methods suggested by RIDEM will be reviewed and evaluated prior to inclusion in a Source Removal Work Plan. Ideally, the type of petroleum distillate that has been disposed of at the site should be determined before an appropriate analytical method can be selected. If a

wide variety of oils has been released, the use of several field screening methods would be quite time consuming. Multiple methods may not produce comparable results because they rely on different means for calibration and detection. However, it may not be possible to find a single reliable method for the determination of total petroleum hydrocarbons (TPH) in soils.

Petroleum hydrocarbons are a diverse group of organic compounds, consisting of aliphatics and aromatics as well as other complex hydrocarbon compounds. As for the laboratory analysis, the two most common laboratory methods used for determination of total petroleum hydrocarbon (TPH) in soil include EPA Method 418.1 (infra red) and 8100 (modified). However, each method has its limitations.

The EPA Method 418.1 (IR) method is commonly referred to as measuring total recoverable petroleum hydrocarbons. This method does not provide any opportunity for identifying the specific organic compounds. There are positive and negative biases with the IR method as well as a high degree of interlaboratory variance in analytical procedures. With the IR method, the total petroleum hydrocarbon measurement is subject to many interferences (naturally occurring organic and vegetative materials). It may not be the best method to use for investigation or remediation verification. An article identifying the limitations of Method 418.1 is enclosed for RIDEM's use.

EPA Method 8100 (modified) is a FID "fingerprinting" method used to measure the concentration of the individual substance of interest rather than the total petroleum hydrocarbon content of the contaminated soil. This method provides useful information in identifying the type of petroleum hydrocarbon, typically in the diesel fuel to motor oil range. However, this method cannot be used to identify lighter petroleum hydrocarbons (e.g. gasoline). A modified EPA Method 8015 (GC) can be used to identify the lighter petroleum hydrocarbons.

Mr. Chris Kellerher of Katahdin Analytical (B&RE's laboratory subcontractor) discussed with Ms. Paula Therrian of the RIDEM UST program, the methods to be used for TPH analysis. There is no specific method identified by RIDEM UST group for TPH analysis. At this time, Ms. Therrian indicated that the preference is for modified Methods 8100 and 8015 for TPH analysis. If the type of petroleum product used is known, then the appropriate analytical method may be selected.

Given the limitations of Method 418.1 and discussions with the RIDEM UST, B&RE proposes to use EPA Method 8010 (modified) for the TPH analysis during this limited evaluation. Since analysis for VOCs would be conducted, it would be possible to use those results to assess aromatic hydrocarbon presence.

Response to Comment 3 RE: Soil piles

As part of the limited source removal evaluation, soils excavated during the test pit program will not be segregated into distinct piles. As discussed during the June 5 conference call, it is the Navy's intention to backfill the test pits on a daily basis to within 15 inches of their surface and then add 15 inches of clean soil (loam) suitable for planting grass.

Stockpiling soils during the limited evaluation phase would be far too time consuming, costly, and would require constant management for such a limited effort. Soil segregation based on a variety of field analytical techniques will require additional work and will be very costly. Given that the area of interest abuts highly active recreational fields, numerous mounds of stockpiled soils would present many potential concerns.

If during potential removal action work soils are to be segregated, plans and precautions will need to be put forth to take into consideration the best method(s) for segregating the soils (depending on previous RI results as well as data collected during the source evaluation), available space for onsite storage, and appropriate measures to avoid migration of potentially contaminated material.

Response to General Comment 3 RE: Poly covering and petitioning the State

During the limited source removal evaluation, appropriate measures will be taken to avoid the spreading or migration of excavated materials from the test pits. The excavated materials will be placed on top of two plies of polyethylene sheeting at each test pit.

As previously stated, it is the intention of the Navy to backfill the test pits with excavated material on a daily basis. Although the Navy does not anticipate the need for stockpiling soils during the source evaluation activity, it is understood that the Navy can petition the State to store excessive soil amounts onsite or at an approved offsite location while alternative disposal options are evaluated.

Response to General Comment 4: (RE: Videotaping)

As discussed on p. 3-6 of the work plan, the types of soils and materials encountered in the test pits will be documented through photographs and videotapes. As requested by RIDEM, copies of the photo and video documentation as well as photocopies of logbook notes would be provided for their use.

Response to Comment 5 RE: Project Objectives

The eight conditions that may warrant a removal action, referred to in the work plan, can be found in 40 CFR Section 300.415, also a public document.

Response to Comment 6 RE: Project Objectives

Petroleum saturated soils will not be investigated as potential source areas during the field investigation. The primary objective of the field investigation and the test pit excavation program, is to evaluate the potential presence of subsurface features such as underground piping, USTs, etc. and to perform a limited assessment of the materials that constitute the on-site mound, near building 144. Petroleum saturated soils presence will be noted, and samples will be collected and will likely be further characterized during a source removal action, if needed. Or, the petroleum saturated soils would be addressed under the RI/FS as part of the long-term management of the site.

Response to Comment 7 RE: Project Objectives

RIDEM will be informed if conditions warrant a source removal action. The Navy will comply with State regulations governing steps for removal actions. Determinations as to whether a time-critical or non-time critical removal action is warranted will be based on conditions observed during the field investigation. There are no plans to implement either type of action prior to conduct of the field evaluation effort.

Response to Comment 8 RE: Schedule

Responses to RIDEM concerns are being addressed in this transmittal.

Response to Comment 9 RE: Schedule

The field work schedule is being modified to accommodate recreational activities planned in the immediate vicinity of the site. At this time, intrusive field investigation activities will be initiated in late June or early July.

Response to Comment 10 RE: Site History

Additional features associated with the former fire fighting use of Site 09 are listed on p. 2-8 of the work plan.

Response to Comment 11 RE: USTs and Associated Piping

Former locations of buildings 134, 135, and 136 are included in the investigation. A flushing trench as well as a lack of sanitary or fuel connections to these structures has been identified on an available drawing. The Navy will attempt to find additional plans for these buildings.

Response to Comment 12 RE: USTs and Associated Piping

The buried piping (containing oily sludge) encountered during the phase II RI may have been in the vicinity of former building 134. Former building locations 134, 135, and 136 will be investigated during the test pit program. Prior to the implementation of field activities, the Navy attempted to locate site-specific plans at NETC's engineering department for the former training facility. No such plans were identified.

Response to Comment 13 RE: On-shore asphalt debris

The implication that the on-shore asphalt debris is the only source of PAHS entering the environment has not been made. The text states that the asphalt on the shoreline and the open face of the fill materials appear to be continuing sources of PAHs. The intent is to determine whether asphalt debris contributes PAHs to the bay. Several other portions of work plan text clearly state that past activities at the training center may have affected various media.

Response to Comment 14 RE: Storm Sewer Outfall

It is the Navy's intention to investigate flow from the outfall pipe as being a possible source of PAH contamination to the environment. In addition, one upstream manhole area will also be investigated in an attempt to corroborate the Phase II RI findings. The objective of this task is to identify whether entrained sediments could result in a "false positive" finding of PAHs in the storm water outfall, as hypothesized in the Draft Final RI Report (TRC, 1994). A recent inspection of the storm drain outfall indicated the presence of a grill and numerous stones (extending from the outfall to approximately 10 feet back). This may prohibit the collection of a sample from the outfall. The lack of precipitation may also prevent the acquisition of a sample since storm water would not be entering the drain.

Response to Comment 15 RE: Location of Potential Buried Piping and Structures

Recent information indicate that vitrified clay pipes have been used beneath some portions of the training facility. If clay pipes were used at the site, then pipe and utility detector proposed for the survey would not likely identify potential contaminant sources, as noted by RIDEM. It is agreed that the lack of detection via a metal detector would not necessarily eliminate an area from investigation. For this limited evaluation, B&RE intends to use the available piping drawings and test pits to attempt to locate such subsurface piping. Also, if the USTs and associated metal piping are identified during the field investigation, then it is reasonable to conclude that clay piping may have been left in place.

Response to Comment 16 RE: Test Pit Excavation Program

The primary objective of this field investigation is to identify potential presence of subsurface structures (sources) that may still contain oils or oily residues. At this time, it is not the Navy's intention to investigate petroleum saturated soils as potential sources of contamination and to fully characterize their extent. If observed, these impacted soils will be documented and sampled. The petroleum saturated soils is considered to be a contaminated medium that may be addressed under a future removal action or under a

long-term remedial action. Petroleum contaminated soils may be further characterized as part of a future removal or remedial action in accordance with applicable State of Rhode Island rules and regulations.

Response to Comment 17 RE: Test Pit Excavation Program

It is the Navy's intent to excavate several test pits to identify and evaluate potential sources of contamination (i.e. USTs, buried piping, etc.). Navy has performed additional research for drawings and plans to better focus the field investigation so that intrusive activities are minimized without resorting to excavating numerous long trenches.

Response to Comment 18 RE: Test Pit Excavation Program

The actual dimensions of the area to be excavated will determine if test pit or test trench is a more applicable term. At this time, the extent of the proposed excavations will be based on potential features encountered, any risk associated with disturbing potentially large oil-filled containers or piping (i.e. creating a release), as well as health and safety concerns with excavation activities.

Equipment requirements for excavation activities have been stipulated in the excavation services technical specification. The Navy appreciates recommendations from RIDEM regarding equipment that was found to be necessary based on previous investigations.

Response to Comment 19 RE: Test Pit Excavation Program

Test pit locations will be determined in the field after a review of the drawings and plans, and review of the utility location survey results. It is the Navy's intent to confirm the presence of subsurface feature. If a removal action is necessary, then a more extensive excavation program would be implemented during the actual removal implementation stage.

Response to Comment 20 RE: Test Pit Excavation Program

At this time, it is the Navy's intent to investigate the probable test pit locations cited in Section 3.4.1 of the work plan. The buried/interior materials of the central mound may include the "christmas-tree" structures and remnants of former buildings (i.e. #130 and #131). By 1975, all structures and facilities associated with the fire fighting training area were demolished, with the exception of the hose house and building 144.

At this time, Navy will review the available plans and determine whether investigation of the western mound is necessary.

Response to Comment 21 RE: Test Pit Excavation Program

It is the Navy's intention to investigate the potential presence of underground piping, as they are associated with the USTs. If these features (metal piping) are identified, then Navy will determine whether additional investigation for non-metallic piping is in order. Navy is aware of the RI's finding of the vitrified clay pipe.

Response to Comment 22 RE: Test Pit Excavation Sequence

The concentrations in the top 1-foot of soil only exceed RI standards for lead in discrete locations for the residential direct exposure criterion. Exceedence of the industrial/commercial exposure criterion is exceeded at one identified location.

All excavated material will be stored on plastic sheeting and appropriate measures will be taken to minimize migration of the soils. The top 15 inches of the test pits will be backfilled with clean soil (loam) to be provided by the excavation subcontractor.

Response to Comment 23 RE: Test Pit Excavation Sequence

The actual depth of the test pits will be determined by the conditions encountered. At this time, the Navy anticipates that test pits will be excavated to the depth of the suspected underground source.

The intent of this investigation is to assess the presence of the underground structures, but not to fully define the associated contaminated soils to identify smear zones or other petroleum related contamination. If contaminated soils are present (identified by presence of underground structures, FID/PID readings, or visual observations), then samples would be collected and appropriately documented through photographs, videotape, and logs. As indicated in Response to Comment 16, the petroleum saturated soils would be more fully characterized under a future removal action (if warranted) or remedial action.

Because of the limited nature of this investigation, and if the opportunity is available, excavation to the water table may be possible. This will be determined in the field

Response to Comment 24 RE: Test Pit Excavation Sequence

It is the Navy's intention to backfill the test pits at the completion of soil sampling, at the end of each day. The site currently has unrestricted access and is used often for recreational activities, as discussed during the June 5 conference call. The objective of this evaluation is to assess potential subsurface features presence and determine the need for a removal action to protect public health or welfare, or the environment. Leaving test pits open 24 hours for the purpose of seeing whether free product forms on the water table is not the primary objective. New monitoring wells to be installed with screens across the water table, will assist identifying potential NAPL presence.

Response to Comment 25 RE: Test Pit Excavation Sequence

Groundwater samples will not be collected from the test pits. Groundwater samples will be collected from newly installed monitoring wells immediately downgradient of potential USTs, underground piping, etc.

Response to Comment 26 RE: Shoreline Sediment Sampling

The time of tidal cycle for the collection of shoreline sediment samples, as well as locations with respect to low and high tide marks will be documented. No test pits will be anticipated to be excavated along the shoreline.

Response to Comment 27 RE: Shoreline Sediment Sampling

Sediment samples will be analyzed for TPH as well as PCBs. However, The TPH analysis would be performed using a modified Method 8015/8010.

Response to Comment 28 RE: Soil Boring and Monitoring Well Installation

Based on review comments from both RIDEM and EPA, three soil borings would be advanced and subsequently three monitoring wells would be installed immediately downgradient of identified subsurface features.

Response to Comment 29 RE: Soil Boring and Monitoring Well Installation

Three monitoring wells will be installed immediately downgradient of potential sources. All well locations will be selected in the field and will be dependent on the location of identified sources. It should be noted that there is an existing network of monitoring wells on site that provides excellent characterization of groundwater. The purpose of these additional wells is to provide water table wells for the assessment of current groundwater conditions, LNAPL evaluations (i.e. groundwater quality), and subsurface soil samples during drilling. If subsurface features are identified during the investigation, then new wells, depending on the configuration of existing wells, would be installed downgradient of those features. B&RE will contact Navy and RIDEM prior to well installation.

Response to Comment 30 RE: Soil Boring and Monitoring Well Installation

For borings that require partial backfilling prior to installing a monitoring well, backfill materials typically include bentonite chips and clean sand. The sand (up to 1-foot thick) is used as a base for the well screen and is NOT mixed with the bentonite chips.

All new wells are to be screened across the water table. The use of bentonite grout/slurry as a backfill material beneath the well screen may not be practical for the following reasons:

1. Bentonite grout, most of the time, is made up of three materials: i.e. water-cement-bentonite. In the past, EPA Region I hydrogeologists have prohibited the use of cement, which is alkaline, below the water table as it may change the pH and therefore alter the water chemistry.
2. Bentonite slurry, typically made up of bentonite and water, may be difficult to place accurately using a tremie pipe. In backfilling, a precise volume of bentonite slurry needs to be placed such that the top of the backfilled interval does not intrude into the desired interval for the well screen. Often, too much slurry is introduced as a backfill material, because of difficulty in pumping a precise volume, and the desired well screen interval is bypassed (covered).
3. Bentonite slurry may also migrate into the formation (making estimating a precise volume difficult), thereby requiring the addition of bentonite chips to the slurry to stop the migration. The use of bentonite slurry may delay the work schedule as the slurry requires 8 to 12 hours (minimum) to set up (i.e. stiffen) prior to introducing materials that will be placed on top of it.

In lieu of bentonite grout or bentonite slurry, it is more practical and less difficult to use bentonite chips and clean sand. Placement is more accurate, and measurement with a weighted tape can provide more accurate backfilling to the desired depths. Bentonite chips expand by absorbing water. The addition of sand to the chips allows water to be more evenly distributed amongst the chips, thereby creating improved hydration and a better seal. In addition, sand with no bentonite is used as a base for the well screen.

Response to Comment 31 RE: Soil Sampling

It is the Navy's intention to field screen soil samples using PID and FID monitoring instruments, and look for visual observations of contaminants. At this time, more intensive field screening analyses such as immunoassay, field GC, etc. are not planned. One of these techniques may be utilized to further characterize the soil if a removal action is warranted. Please refer to the response for general comment no. 3 for more information.

Response to Comment 32 RE: Soil Sampling

One soil sample will be collected from each boring in the area above the water table (i.e. the smear zone). Although RIDEM recommends the collection of a second sample from the most contaminated zone in the boring, the Navy anticipates that this sample will be collected from the test pit of an identified source. As previously stated, each of the three borings will be located immediately downgradient of an identified source.

Thus, representative soil samples from the most contaminated zone in the test pit and from the smear zone in the soil boring will have been collected.

Response to Comment 33 RE: Groundwater Sampling

If free product is encountered during groundwater sampling, then a specimen will be collected for laboratory analysis of TCL organics (VOCs, SVOCs, PCBs) and petroleum hydrocarbon fingerprinting.

Response to Comment 34 RE: Storm Sewer Outfall Sampling

The Navy anticipates that storm sewer sampling will occur during a period of outflow (i.e. low tide) from the pipe. In addition, the Navy will collect an aqueous sample from a catch basin upstream of the site, preferably several hours after a storm event. The Navy does not anticipate collecting sediment samples from the upstream location or from the area below the discharge point of the pipe.

Response to Comment 35 RE: Storm Sewer Outfall Sampling

The Navy anticipates investigating the storm sewer outfall as proposed in the work plan. The objective of this activity is to assess the current status of discharge of PAH constituents from the storm sewer. During the evaluation, the Navy does not anticipate inspecting storm sewer pipes or backfill around pipes to identify potential areas of groundwater infiltration or the potential for pipes to act as conduits for contaminant migration.

[REDACTED]

Hydrocarbon Contaminated Soils

Volume IV

Perspectives
Analysis,
Human Health and Risk Assessment
Remediation

Edward J. Calabrese
Paul T. Kostecki
Marc Bonazountas



Amherst, Massachusetts

[REDACTED]

Hydrocarbon contaminated soils/ Edward J. Calabrese, Paul T. Kostecki, Marc
Bonazountas, editors
ISBN 1-884940-00-5

COPYRIGHT © 1994 by Amherst Scientific Publishers (ASP)

Neither this book nor any part may be reproduced or transmitted in any form or
by any means, electronic or mechanical, including photocopying, microfilming,
and recording, or by any information storage and retrieval system, without
permission in writing from the publisher.

This book represents information obtained from authentic and highly regarded
sources. Reprinted material is quoted with permission and sources are indicated.
A wide variety of references are listed. Every reasonable effort has been made
to give reliable data and information, but the editors and the publisher cannot
assume responsibility for the validity of all materials or for the consequences of
their use.

Amherst Scientific Publishers
150 Fearing Street, Amherst, Massachusetts 01002

PRINTED IN THE UNITED STATES OF AMERICA

"There is limited industry, and t soil...contamination is generally unawa liabilities they in contamination."

This statement op
"Environmental and Pub
conference in 1985. The
contaminated soils and
respect to addressing the
with petroleum contamin.

It is the 1990s. The
and characterizing; we ar
our companies and custo
the 1990s, we, as a natio
addressing the environm
petroleum contaminated s

The 1985 and subse.
fate of petroleum in soil :
state-of-the-art field meas
contaminated soils, and p

Today we seek spe
experimenting and using
solutions; and we are fin
standards and questioning
papers included in this yea
site sensors for long term r
devices for site screenin
immunoassay technology t
washing process for remed
demonstrate progress accor
tool to determine "how clea
in search of a better gauge

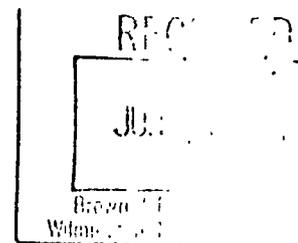
The evolution of the i
we once spent countless
characterize a site's contam
The developments in data c
technology, coupled with
continual changes in the
capabilities and confidence
designing and implementing

Base in New Hampshire,⁶ and provided data that correlated with samples measured with a photo-ionization detector.

Commercialization of this sensor/instrument system is being pursued by Ariano Technologies, Inc..

REFERENCES

1. Spittler, T. M., *Field Instrumentation Uses and Needs of U.S. EPA*, presented at the Symposium on Field Screening for Environmental Pollutants, Massachusetts Institute of Technology, Cambridge, MA, October 26, 1992.
2. Devitt, Dale A., et al, *Soil Gas Sensing for Detection and Mapping of Volatile Organics*, National Water Well Assn., Dublin, OH, 1987, 3.
3. M. A. Portnoff, R. Grace, A. M. Guzman, and J. Hibner, *Measurement and Analysis of Adsistor and Figaro Gas Sensors Used for Underground Storage Tank Leak Detection*, presented at the American Institute of Chemical Engineers 1991 Summer National Meeting, Pittsburgh, PA, August 18-21, 1991.
4. G B. Wickramanayake, R. E. Hinchee, J. A. Kittel, N. G. Reichenbach, and B. J. Nielsen, *Evaluation of External Vapor Monitoring Devices for Underground Petroleum Products Storage Tanks*, Hazardous Materials Control, Sept/Oct 1991, P. 32-40.
5. Klainer, S. M., et al, *Proceedings of the Symposium on Field Screening Methods for Hazardous Waste Site Investigations*, October, 1988, Las Vegas, P. 25.
6. Barnard, S. M., Walt, D. R., *Environ. Sci. Technol.* 1991, 25, 1301-1304.
7. Lakowicz, J. R., *Principles of Fluorescence Spectroscopy*, Plenum Press, New York, 1983, P. 189-208.
8. Devitt, Dale A., et al, op.cit., P. 75.
9. Devitt, Dale A., et al, op.cit., P. 64.
10. Prof. Gary Robbins, University of Connecticut, Storrs, CT; personal communication.
11. de Filippi, R. P., and Cody, T. J., *A Monitoring System for Hydrocarbon Leakage from Petroleum and Petrochemical Products Sites*, Presented at the Third International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Feb. 26, 1993, Las Vegas, Nevada.



CHAPTER 8

Bias Associated With the Use of EPA Method 418.1 For the Determination of Total Petroleum Hydrocarbons in Soil

Scott George, PG, CHMM, Environmental Science & Engineering, Inc., St. Louis, MO

INTRODUCTION

EPA Method 418.1, originally intended solely for use with liquid waste, has been one of the most widely used methods for the determination of total petroleum hydrocarbons (TPH) in soils. At last count, approximately 19 states use or permit the use of Method 418.1 for the determination of "action" or cleanup levels for petroleum contaminated soils.¹ In some cases, Method 418.1 is the sole criteria for verification of site cleanup. Method 418.1 has been "modified" for determining TPH concentrations in soil between states or laboratories with no consistency to the modifications. The EPA had proposed draft Method 9073, which was expanded to include soils, that specified Soxhlet extraction for solid samples and suggested the use of the petroleum product in question as a standard. EPA has withdrawn this method. Draft Method 9073 clearly stated that the method is not applicable for the measurement of gasoline range organics.

Several areas of concern are associated with the use of Method 418.1, as it is commonly used. The concerns can be broken into two principle areas: (1) inherent inaccuracies in the method (i.e., positive and negative biases); and (2) the high degree of interlaboratory variance in standard operating procedures. Although Method 418.1 can still be useful in some site assessments, great care must be taken in the selection of the extraction and cleanup procedures and in the interpretation of the analytical results. All analytical procedures have a degree of variance and problems associated with interpretation of results. Method 418.1, however, has a greater degree of variance among laboratories and more uncertainty in interpretation than most analytical procedures.

This chapter presents some of the problems associated with Method 418.1 and briefly describes the reasons for the use of the newer gas chromatographic (GC) methods for TPH determination in soil. As part of this study, the Method 418.1 standard operating procedures (SOPs) from five laboratories in two states were reviewed. A limited study of analyses of split samples was performed among three laboratories to determine if natural organics or industrial

waste products could cause positive biases in Method 418.1. Results obtained from other studies of Method 418.1 are also presented.

PETROLEUM CHEMISTRY

Petroleum products consist of complex mixtures of organic compounds. The individual constituents cover a broad range of boiling points, carbon numbers, chemical families, and structural isomers. The typical petroleum fractions, carbon ranges, and distillation temperatures are presented in Table 8.1 and Figure 8.1.^{2,3} The hydrocarbon groups present in petroleum products include: alkanes, alkenes, alkynes, aromatics, polynuclear aromatics, and complex hydrocarbon compounds containing oxygen, nitrogen, and sulfur. Petroleum products also contain trace amounts of elements such as bromine, cadmium, nickel, and vanadium. The hydrocarbon groups present in petroleum products are presented in Figure 8.2.

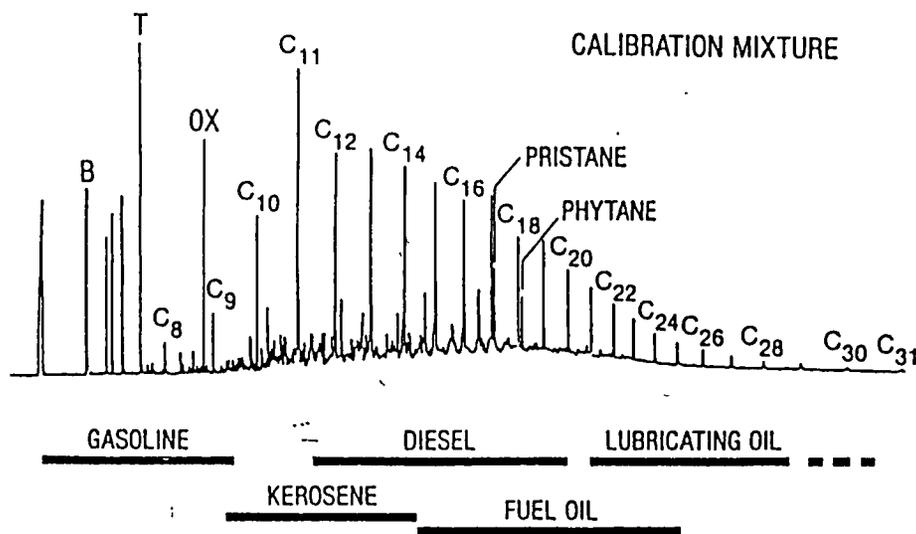


Figure 8.1. Approximate carbon number ranges for individual hydrocarbon products³.

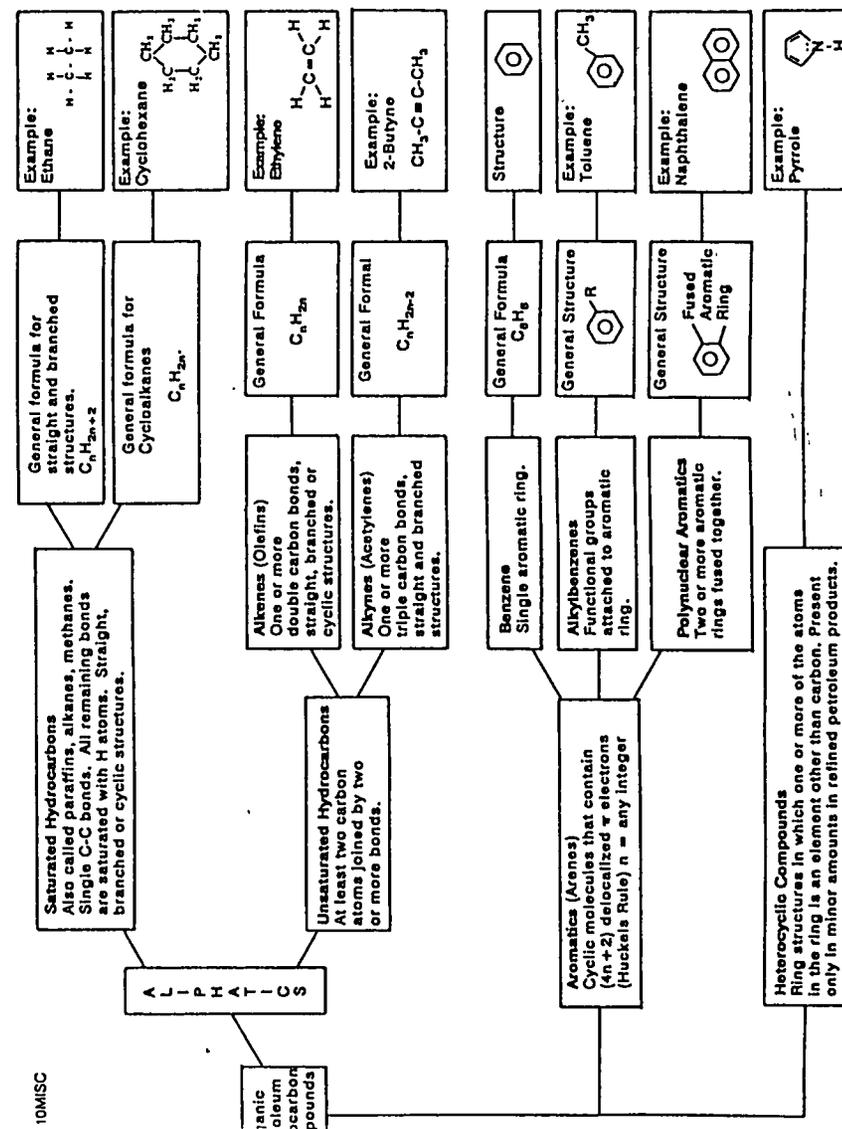


Figure 8.2. Organic petroleum hydrocarbon compounds.

Table 8.1. Petroleum Distillation Products²

| Fraction | Distillation Temperature, °C | Carbon Number |
|---------------------------|------------------------------|---|
| Gas | Below 20 | C-1 to C-4 |
| Petroleum Ether | 20 to 60 | C-5 to C-6 |
| Ligroin (light naphtha) | 60 to 100 | C-6 and C-7 |
| Natural Gasoline | 40 to 205 | C-5 to C-10 and Cycloalkanes |
| Kerosene | 175 to 325 | C-12 to C-18 and aromatics |
| Gas Oil | Above 275 | C-12 and higher |
| Lubricating Oil | Non-volatile liquids | Probably long chains attached to cyclic compounds |
| Asphalt or Petroleum Coke | Non-volatile solids | Polycyclic structures |

Upon distillation of petroleum crude, specific families of organic compounds will concentrate into each of the fractions. Petroleum "cracking" and other refinery processes are also used to alter the petroleum constituent structures into more useable compounds. General ranges of hydrocarbon groups in petroleum products are shown in Table 8.2⁴

Table 8.2. Hydrocarbon Group Types in Petroleum Products⁴

| Product | % Composition | | |
|----------------|---------------------|-------------------|-----------|
| | Saturates (Alkanes) | Olefins (Alkenes) | Aromatics |
| Gasolines | 36 to 71 | 5 to 13 | 22 to 54 |
| Jet fuels | 78 to 85 | < 1 to 4 | 16 to 25 |
| #2 fuels | 48 to 57 | ? | 33 to 38 |
| Diesel fuel | 78 | 2 | 20 |
| Kerosene | 68.6 | ? | 19.4 |
| Lube oils | 68 to 90 | ? | 10 to 32 |
| Residual fuels | ? | ? | ? |

Although general ranges for boiling points, carbon numbers, and petroleum hydrocarbon groups in the different petroleum distillates can be given, a high degree of chemical variability exists in refined petroleum products. The sources of this variability include:

- Origin of the crude oil;

- Different distillation and refinery processes;
- Blending of additives and octane boosters;
- Seasonal changes in formulation designed to moderate fuel volatility;
- Blending of products by independent retailers; and
- Structural isomers of the individual petroleum constituents.⁵

In addition, several factors will affect the composition of petroleum products when released into the environment (volatilization, partitioning between liquid and solid phases, and biodegradation).

Therefore, chemical analysis for the determination of petroleum products released into the environment poses complicated analytical challenges. Each of the hydrocarbon groups mentioned can have different solubility in extraction solvents and different responses to analytical instrumentation. EPA Method 418.1 has been used as a "catch-all" to cover the broad range of possible chemical constituents in the various petroleum products. As will be discussed, no single method can be considered a reliable test for TPH concentrations in soils. If at all possible, the type of petroleum distillate (i.e., gasoline, diesel, cutting oil) that has been released should be known before an appropriate analytical method can be chosen.

DESCRIPTION OF METHOD 418.1 WITH INTERLABORATORY COMPARISON

An evaluation of the biases associated with Method 418.1 begins with a description of the test procedure. Method 418.1 was originally intended only for aqueous samples not soils. It has been widely modified, however, for the determination of TPH in soil. There has been no standard set of modifications used, allowing for significant differences between laboratories in SOPs. The following is a general description of the test procedure with some of the variances discovered among laboratories.

Step 1--Sample Preparation and Extraction

The first step performed by most laboratories in the extraction procedure is homogenization of the sample by grinding or mixing. The determination of the moisture content is performed on a separate aliquot of the sample. Sample sizes range from 20 to 50 grams with smaller aliquots taken if the concentration of petroleum is high. One of the laboratories in this study adds 1.0 milliliter (ml) of 1:1 hydrochloric acid (HCl) to an approximate 40 gram sample reportedly to enhance the Freon-113 solubility of polar hydrocarbons. All of the laboratories add granular anhydrous sodium sulfate (Na_2SO_4) to remove moisture. Generally, no specifications are given on the mass of Na_2SO_4 added other than a sufficient amount to form a sandy texture. One laboratory adds 50 grams of Na_2SO_4 to a 50-gram sample. Another laboratory adds 10 grams of Na_2SO_4 to a 20-gram soil sample.

The common solvent used for extraction is Freon-113 (1,1,2-trichloro-1,2,2-trifluoroethane). As a nonpolar solvent Freon-113 will preferentially extract nonpolar constituents from the soil matrix (i.e., petroleum hydrocarbons). However, it will also extract some polar organic compounds. A variety of polar organic compounds are present naturally in soils and will codissolve with the non-polar petroleum hydrocarbons. Many of the heavy weight petroleum fractions have poor solubility in Freon-113. The extraction of the heavy weight petroleum can be ameliorated if the Soxhlet extraction method is used [at the expense of losing low boiling point (LBP) fractions].

After the initial sample preparation, the extraction procedures vary widely between laboratories and are probably the single greatest factor affecting interlaboratory variability. Four different types of extraction procedures were found to be in use under the generic Method 418.1: chromatography column, tumbling, sonication, and Soxhlet extraction.

Column Method

One of the laboratories placed the mixture of Na_2SO_4 and soil into a 19 mm x 30 mm glass chromatograph column with glass wool and a stop-cock valve at the bottom. One hundred ml of Freon-113 are poured through the column and collected into a beaker. In general, this method appears to be a poor extraction procedure. The Freon-113 does not contact the soil matrix in a uniform manner. "Channeling" of Freon-113 as it passes through the column can prevent sufficient contact time.

Rotary Agitation

One of the laboratories extracted the soil samples by rotation for four hours. A 20-gram sample is mixed with 10 grams of Na_2SO_4 and 100 mL of Freon-113 in a 250-ml glass bottle. The mixture is rotated end-over-end for four hours, followed by decanting the solvent into a 20-ml scintillation vial. Three-tenths gram of silica gel (specified only as 60-200 mesh) is added to the vial prior to the solvent addition. The vial is loaded onto a mechanical shaker and agitated for five minutes. No specification is given for settling time. The sample is filtered into a clean, dry scintillation vial.

Sonication

The sonication methods are based on EPA Method 3550. After sample preparation, the sample is mixed with Freon-113 and disrupted with an ultrasonic probe. The length of sonication is two minutes. Method 3550 specifies a two minute extraction time for high concentration samples and three minutes for low concentration samples. A study performed by Orion Laboratories found this to be an ineffective extraction method for some petroleum products.⁵ The EPA has

also found this to be ineffective, leading to the requirement of Soxhlet extraction in the draft Method 9073 (withdrawn).

Soxhlet

The Soxhlet extraction method is based on EPA Method 9071.⁴ The prepared sample is placed into an extraction thimble. A glass wool plug is placed on top of the sample. A Soxhlet extractor allows heated Freon-113 to reflux through the sample in a partially closed system repeatedly at approximately 20 times an hour for a minimum of four hours. One laboratory specified that if the Freon-113 filtrate from the thimble was not colorless after four hours, the extraction should continue until the Freon-113 appeared colorless.

Step 2--Sample Cleanup

Since polar organic compounds, such as grease, vegetable oils, fats, waxes, and polyfunctional compounds, are co-dissolved with the petroleum hydrocarbons in Freon-113, a silica gel cleanup step is required to remove the interferences. If the cleanup step is not performed, the results are reported as total recoverable oil and grease (EPA Method 413.1). The silica gel consists of precipitated silicic acid in the form of lustrous granules. The chemical formula is H_2SiO_3 .

The silica gel specified in Method 418.1 is 60-200 mesh (Davidson Grade 950 or equivalent). Davidson Grade 950 has been out of production for approximately 10 years. Davidson Grade 923, with a surface area of 500 m^2/gm , is a common replacement.

Many factors will affect the efficiency of the silica gel in removing the interferences:

- Grade of silica used--One of the laboratories used Davidson Grade 62 with a surface area of 343 m^2/gm . Using silica gel with less surface area could cause the silica gel to be less efficient in removing the polar compounds.
- Quantity of silica gel--the laboratories added between 1.5 grams for a 20-gram sample to 3 grams for a 50-gram sample. It is possible that the absorption capacity of the silica gel could be exceeded. The original 418.1 method suggested that the absorbance capacity of the silica gel "could" be tested by adding additional gel and redetermining the infrared (IR) absorbance. The draft Method 9073 (withdrawn) specified that the silica gel absorbance must be tested. None of the laboratories connected with this study determined if the absorbance capacity of the silica gel had been exceeded. One of the laboratories does not perform the silica gel cleanup, but reports the results as TPH, not oil and grease.
- Deactivation--The test procedure calls for the silica to contain 1 to 2 percent water as defined by a residue test at 130°C. Most laboratory

SOPs contain no information on the preparation of the silica gel. If the silica gel is not deactivated, it could remove small quantities of petroleum hydrocarbons as well as the interferences. If the silica is deactivated with too much water, it may not remove any of the interferences.

Settling time--Most of the laboratories did not specify the length of time allowed for the silica gel to absorb interferences and settle. One laboratory specified a two hour minimum waiting period. Most laboratories run the sample analysis five minutes after addition of the silica gel, which may not be a sufficient time period for the silica gel to act.

Step 3--Quantification

After the silica gel has been added, the Freon-113 absorbance of TPH in Freon-113 is measured on an IR spectrophotometer at a wave length of approximately $2,950\text{ cm}^{-1}$. Several of the laboratories specify $2,930\text{ cm}^{-1}$. Several of the laboratories set the IR at $2,930\text{ cm}^{-1}$ (or $2,950\text{ cm}^{-1}$) and read the percent transmission. The other laboratories scan a general region around $2,930\text{ cm}^{-1}$, find the maximum peak in the standard, and use this response in calculating the calibration curve and sample results. If the IR is set at one specific wavelength, it may not be reading the maximum absorbance peak, but one of the peak shoulders. The use of one setting could lead to high or low results depending on the sample curve in the region of that specific wavelength.

Step 4--Standards

For comparison, a mixture of 15.0 mL n-hexadecane (normal chain alkane), 15.0 mL isooctane (branched alkane), and 10.0 mL chlorobenzene (aromatic) is used. Draft Method 9073 (withdrawn) specifies that a sample of the product in question be used, if possible, as the standard (i.e., diesel, fuel oil, etc.). If a sample of the petroleum product is not available, the above mixture is used. All of the laboratories contacted in this study used the standard mixture, not the petroleum product in question.

POSITIVE AND NEGATIVE BIASES

Extraction Methods

The type of soil in which the petroleum hydrocarbons are contained will have an effect on the extraction process and the percent recovery of the petroleum. This problem is, of course, not unique to Method 418.1. Any type of extraction will tend to be more effective in a sandy soil compared to a high clay content soil due to the difficulty in discharging the clay sized particles.

Sonication and column extraction methods are commonly used with Method 418.1 and tend to be inefficient with tight soils.

A limited study by Orion Laboratories performed with soil affected by heavy weight petroleum products obtained the results shown on Table 8.3 when comparing sonication versus Soxhlet extraction.⁶

Table 8.3. Comparison of Sonication and Soxhlet Extractions⁶

| Soil Description | TPH mg/kg by Method 418.1 | |
|------------------------|---------------------------|---------|
| | Sonication | Soxhlet |
| Sand/Petrol Odor | <10.0 | 595.0 |
| Clay | <10.0 | 342.2 |
| Silt/Sheen/Petrol Odor | <10.0 | 132.5 |
| Sand/Gravel | <10.0 | 211.7 |
| Wet/Petrol Odor | <10.0 | 81.7 |
| Gray Sand | <10.0 | <10.0 |
| Moist Sand | <10.0 | <10.0 |
| Clay/Sand | <10.0 | 84.6 |
| Fine Sand | <10.0 | 837.7 |
| Silty Clay | <10.0 | 42.4 |
| Clay | <10.0 | 234.8 |

Clearly, the Soxhlet method obtains a more thorough extraction. The problem is that most (if not all) of the LBP hydrocarbons are removed in the extraction process, making this an inappropriate extraction method for LBP hydrocarbons. The draft Method 9073 (withdrawn) which calls for a Soxhlet extraction for soils states, "This method is not applicable to the measurement of gasoline." The chromatographic column is likely the most inefficient process of the commonly used extraction methods. As stated earlier, "channeling" of the Freon-113 as it passes through the column and failure to disburse the soil particles can prevent proper Freon-113/soil contact.

Distinctly different results will be obtained depending on the extraction method chosen. Negative biases for high boiling point hydrocarbons can occur if an ineffective extraction method (chromatography column) or extraction time (sonication -- 2 minutes) are chosen. Negative biases for LBP hydrocarbons will occur if a thorough extraction method (Soxhlet) or a long extraction time is used.

Biases Due to Standards

The relative response of the IR spectrophotometer is based on the amounts of the different hydrocarbon types present (i.e., aromatics, alkanes, etc.). The reference oil standard is a constant mixture of 37.5 percent n-hexadecane (normal chain alkane), 37.5 percent isooctane (branched alkane), and 25 percent chlorobenzene (aromatic) (Figure 8.3).⁷ Therefore, if a disparity exists between the chemical composition of the calibration standard and the sample, positive or negative biases will result. The reference oil standard has the best comparison to a middle distillate petroleum product (i.e., diesel, with approximately 75 percent alkanes and approximately 25 percent aromatics). The more the petroleum product component groups (alkanes, aromatics) vary from the reference oil, the higher the analytical biases.

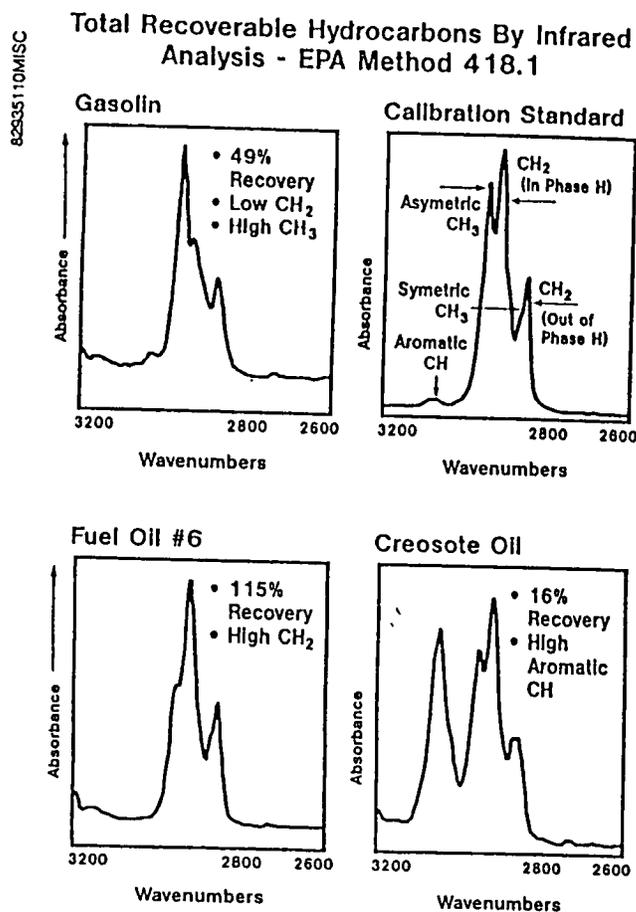


Figure 8.3. IR absorbance patterns of a calibration oil, gasoline, fuel oil #6, and creosote vs. wavenumber (2600 to 3200 cm^{-1}). These samples were prepared in Freon and analyzed according to EPA Method 418.1 using a quantification absorbance at 2930 cm^{-1} .⁷

A limited study conducted by Groundwater Analytical, Inc. demonstrated accuracy errors attributed by the authors to the IR spectral disparity between the product sample and the standard (Table 8.4)⁸. As can be seen, the lowest percent relative error is for diesel fuel.

Positive and Negative Biases Due to the Silica Gel Cleanup

As stated above, silica gel effectiveness will depend on the type and quantity of silica gel used, preparation procedures, and the time allowed for the gel to absorb interferences. In addition, both nonpolar (normal alkanes) and relatively polar compounds are present in petroleum (aromatics and aromatics with functional groups attached). Therefore, it is possible that negative bias could be introduced by the removal of relatively polar hydrocarbons by the silica gel. The degree of bias will depend (in addition to the silica gel factors listed above) on the percentage of nonpolar to relatively polar compounds present in the petroleum product. The author is unaware of any studies of negative bias due to silica gel removal in Freon-113 extracts of soils. Groundwater Analytical, Inc. performed a study of the effects of silica gel suppression on Freon-113 extracts of petroleum saturated aqueous solutions (Table 8.5).⁸ The silica gel negative biases would be expected to be higher in aqueous solutions due to the preferential solution of the polar hydrocarbons in water. The results of the Groundwater Analytical, Inc. study indicate significant negative biases. The bias appears to be greatest in high molecular weight (long chain and aromatic hydrocarbon) products.

The author is unaware of studies showing the effectiveness of the silica gel in removing nonpetroleum interferences. Several studies, however, have reported the ineffectiveness of the silica gel.

Biases Due to the Presence of Industrial or Natural Materials

IR spectroscopy quantifies the vibration (stretching and bending) that occurs when a molecule absorbs electromagnetic energy in the IR region of the electromagnetic spectrum.⁹ The IR absorption spectrum between 5,000 and 1,250 cm^{-1} is attributed to vibrational stretching and bending of various functional groups.

The IR absorption wave length depends on the bond type and the strength of the bond (i.e., single carbon bonds absorb at 1,200 cm^{-1} and triple carbon bonds absorb at approximately 2,200 cm^{-1}). Different functional groups and bond types have different IR absorption wave lengths and intensities. For example: aromatic Ar-H stretching exhibits an absorption at approximately 3,300 cm^{-1} , and carboxylic acids absorb IR radiation at 2,500 to 3,000 cm^{-1} (O-H stretching).¹⁰ The range of approximately 2,900 to 3,000 cm^{-1} corresponds to stretching of C-H bonds. Therefore, an IR spectrum over a wide range is unique for a given compound and can be used to fingerprint unknowns.

Table 8.4. Accuracy evaluation of the reference oil standard and the TPH-IR Method (modified from reference #8).

| PETROLEUM PRODUCT | CONCENTRATIONS (mg/L) | | RELATIVE % ERROR | | | | | | | | | |
|---------------------------|-----------------------|---|------------------|-----|-----|-----|-----|---|-----|-----|-----|--|
| | ACTUAL | MEASURED (AFTER SILICA GEL ADDITION) | -50 | -40 | -30 | -20 | -10 | 0 | -10 | -20 | -30 | |
| PREMIUM UNLEADED GASOLINE | 30 | 15.2 | -48% | | | | | | | | | |
| FUEL OIL NO. 2 | 30 | 34.1 | -14% | | | | | | | | | |
| DIESEL FUEL | 30 | 31.6 | 5.3% | | | | | | | | | |
| FUEL OIL NO. 4 | 30 | 22.0 | -27% | | | | | | | | | |
| TRANSMISSION OIL | 30 | 39.8 | -33% | | | | | | | | | |
| 10W-30 MOTOR OIL | 30 | 40.4 | -35% | | | | | | | | | |
| 80W-90 GEAR OIL | 30 | 39.7 | -32% | | | | | | | | | |

- Each solution was prepared by adding 30 mg of petroleum product to 100 mL of Freon-113. Concentration of each Freon-113 solution was measured prior to the addition of silica gel and after the addition of silica gel.
- Measured concentrations were calculated on the basis of the absorbance of the Reference Oil at 2930 cm^{-1} .

Table 8.5. Effect of silica gel on freon-113 extracts of petroleum saturated aqueous solutions (modified from reference #8).

| PETROLEUM PRODUCT | CONCENTRATIONS (mg/L) | | RELATIVE % ERROR | | | | | | | | | |
|---------------------------|------------------------------|---------------------------|------------------|-----|-----|-----|-----|-----|-----|-----|-----|---|
| | PRIOR TO SILICA GEL ADDITION | AFTER SILICA GEL ADDITION | -90 | -80 | -70 | -60 | -50 | -40 | -30 | -20 | -10 | 0 |
| PREMIUM UNLEADED GASOLINE | 34.4 | 12.6 | -37% | | | | | | | | | |
| REGULAR UNLEADED GASOLINE | 40.8 | 27.4 | -33% | | | | | | | | | |
| FUEL OIL NO. 2 (A) | 18.9 | 12.3 | 27% | | | | | | | | | |
| FUEL OIL NO. 2 (B) | 10.6 | 10.4 | -1.8% | | | | | | | | | |
| DIESEL FUEL (A) | 7.8 | 5.0 | -36% | | | | | | | | | |
| DIESEL FUEL (B) | 6.0 | 3.9 | -35% | | | | | | | | | |
| FUEL OIL NO. 4 | 3.1 | 1.3 | -58% | | | | | | | | | |
| TRANSMISSION OIL | 5.1 | 1.9 | -63% | | | | | | | | | |
| 10W-30 MOTOR OIL | 30.4 | 4.3 | -86% | | | | | | | | | |
| 80W-90 GEAR OIL | 38.8 | 5.3 | -86% | | | | | | | | | |

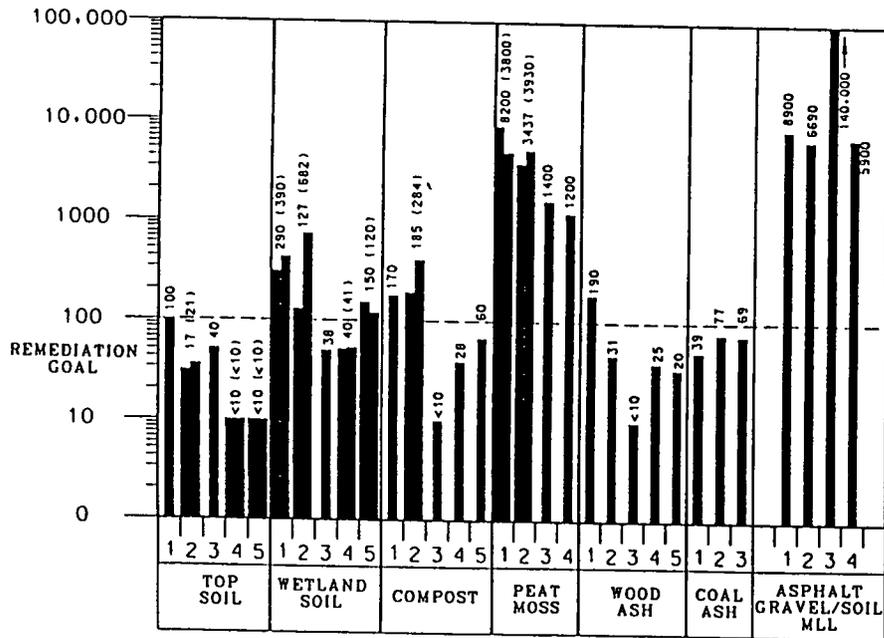
- Saturated aqueous solutions of each petroleum product were prepared. Each saturated aqueous solution was then extracted with Freon-113. The concentration of each Freon-113 extract was measured prior to the addition of silica gel and after the addition of silica gel.
- Measured concentrations were calculated on the basis of the absorbance of the Reference Oil at 2930 cm^{-1} .

One of the principle problems of Method 418.1 is that many compounds have IR absorption peaks in the $2,950\text{ cm}^{-1}$ region of the spectrum. Any scan of a book of IR spectra will show innumerable compounds with a positive IR absorption around $2,950\text{ cm}^{-1}$ (Figure 8.4).¹¹ Many of these compounds (principally carboxylic acids and hydrocarbons) have been found at high concentrations occurring naturally in soil.¹² The IR spectra of humic acids from terrestrial soils and marine sediments is presented in Figure 8.5.¹³ The IR region around $2,950\text{ cm}^{-1}$ clearly shows absorbance for humic compounds.

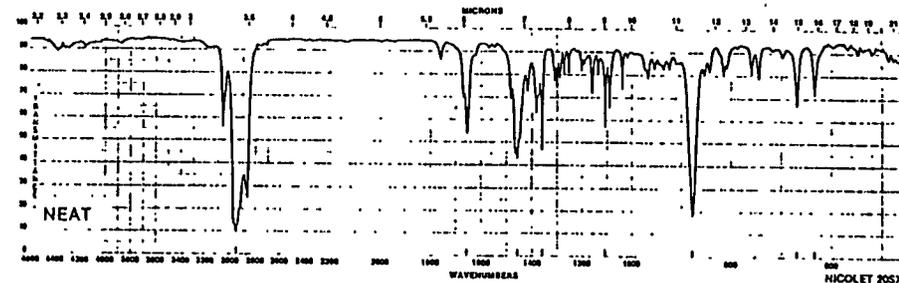
Since only the IR region around $2,950\text{ cm}^{-1}$ is scanned in Method 418.1, a fingerprint of the compound cannot be obtained and identification is not possible. The IR absorbance spectra in the region of $2,950\text{ cm}^{-1}$ of several materials are shown in Figure 8.6. Although the relative intensity may vary, there are no distinctive characteristics that would allow the analyst to make a judgement on the nature of the material.

Polar compounds are theoretically removed with the silica gel cleanup, leaving behind only nonpolar petroleum hydrocarbons. The silica gel cleanup, however, appears to be inefficient. None of the laboratories in this study routinely check if the absorbance capacity of the silica gel has been exceeded. To test the theory that naturally occurring organics and commonly encountered industrial products will cause positive biases by Method 418.1, a group of these materials was collected, mixed thoroughly in a stainless steel bowl, and separate aliquots sent to three laboratories. The samples were marked to indicate normal soil boring samples (i.e., Boring 5 at 12 to 15 feet). The results of the study are presented in Table 8.6.

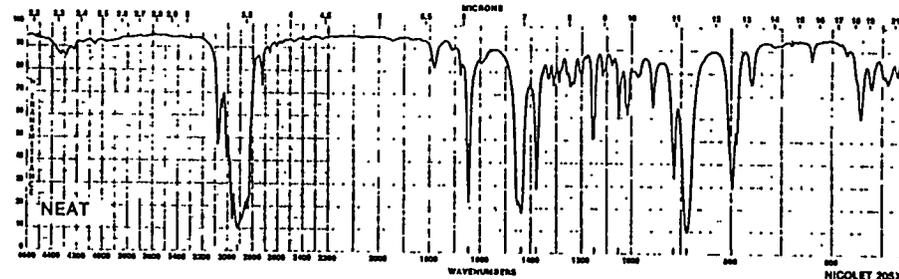
Table 8.6. Total Petroleum Hydrocarbons (mg/kg) by Method 418 1 of Natural Organic and Industrial Materials.



(+) Camphene, 80%



(S)-(-)-Limonene, 92%



Gallic acid, 97%

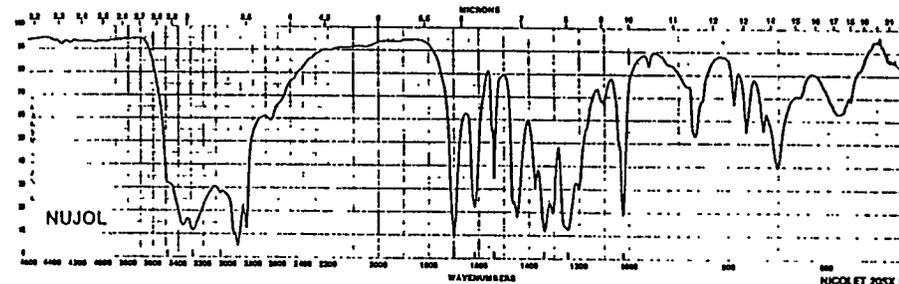


Figure 8.4. IR spectra of naturally occurring organic chemicals.

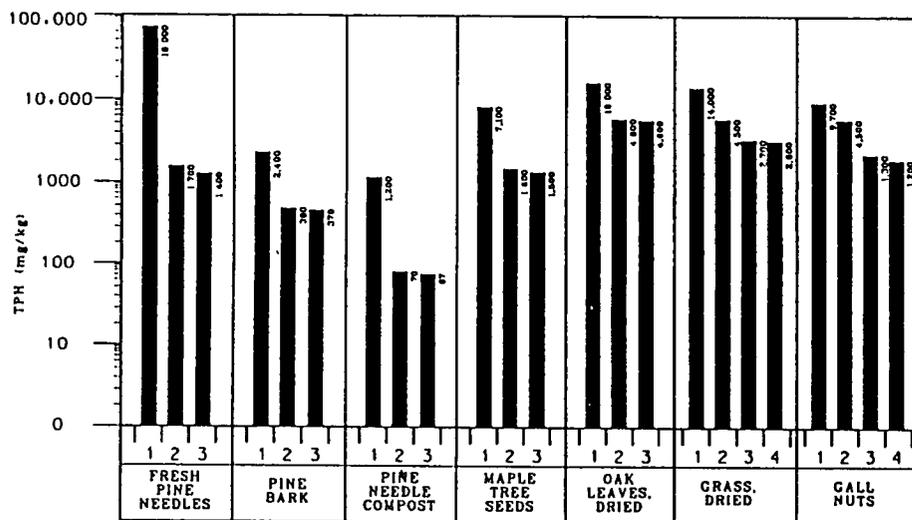
As can be seen from Table 8.6 and Figure 8.6, it is possible for nonregulated industrial materials and natural organics to be confused with regulated petroleum products.

Other studies have also noted the occurrence of false positives due to natural organics. A study performed by Groundwater Analytical, Inc. showed significant false positives in natural materials (Table 8.7).⁸

Although sequential additions of silica gel did tend to lower the TPH concentrations, some materials still contained high levels of TPH after three additions of silica gel (i.e., dried grass). Clearly, the silica gel is inefficient at removing these interferences.

Block, Clark & Bishop did a comparison of TPH concentrations in soil measured by IR and GC as part of the assessment of the biological treatment of soils. The results of the comparison are shown in Table 8.8.¹⁴ The GC results were consistently lower.

Table 8.7. Effect of silica gel on freon-113 extracts of vegetative materials (modified from reference #8)



- 1 Prior to Addition of Silica Gel
- 2 After First Addition of Silica Gel
- 3 Second Addition of Silica Gel
4. After Third Addition of Silica Gel

NOTE

Each vegetative material was extracted with Freon-113. The concentration of each Freon-113 extract was measured prior to the addition of silica gel, and after the addition of silica gel, and then again after a second addition of silica gel. A third addition of silica gel was performed only for the Dried Grass and Gall Nuts extracts, due to the significant change in concentration caused by the second addition of silica gel. Measured concentrations calculated on the basis of the absorbance of the Reference Oil at 2,930 cm^{-1} .

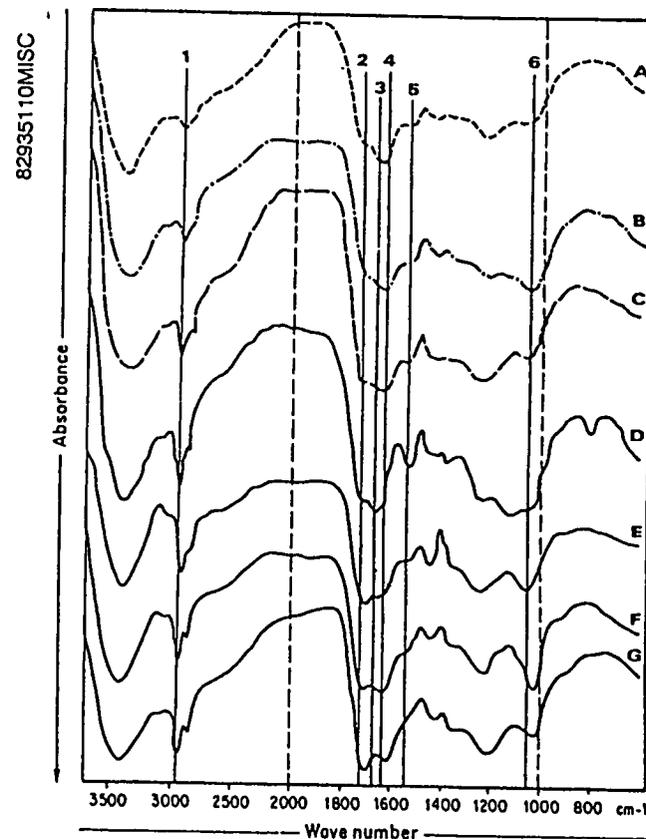


Figure 8.5. Comparison of IR spectra of humic acids from terrestrial soils, and humic acids from recent marine sediments. Identification of humic acids: *Terrestrial soils*: A rendzin, B brown soil, acid, C podzol. *Marine sediments*: D and F France, Atlantic coast, E Eastern Mediterranean, G West Africa. Identification of IR bands: 1 aliphatic C-H, 2: C=O, 3 and 5 amides, 4 aromatic C=C, 6 C-O of polysaccharides.¹³

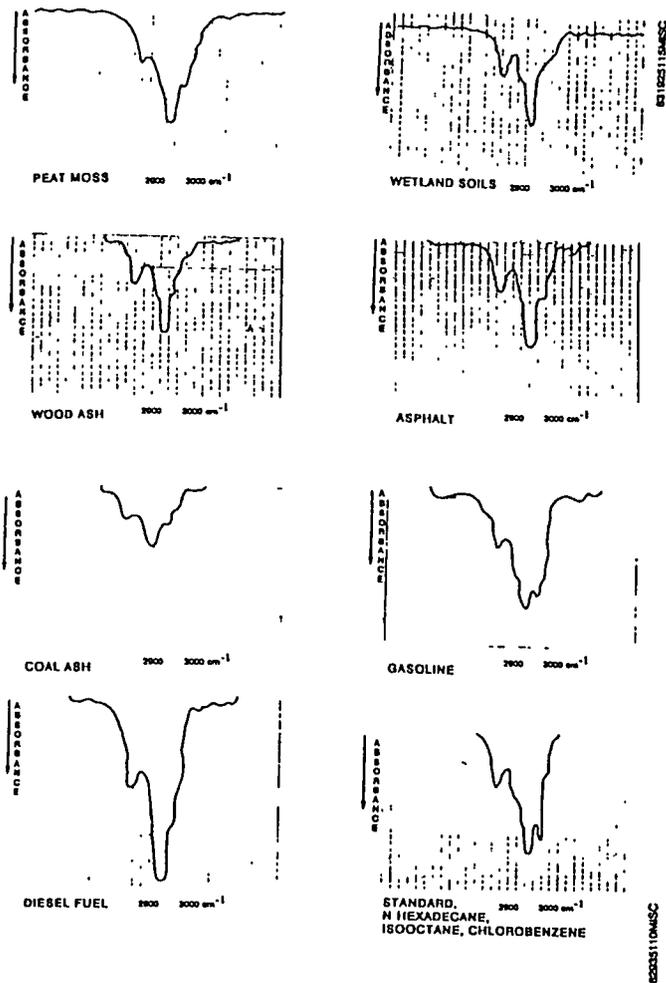


Figure 8.6. Infrared absorbance spectra for various materials.

Table 8.8. Comparison of TPH analyses IR and GC methods.¹⁴

| Sample | Location | TPH (mg/kg) | |
|----------|-----------------------|-------------|-------|
| | | By IR | By GC |
| I-AB.1.5 | Treatment window | 317 | 69 |
| I-CD.1.5 | Treatment window | 148 | 109 |
| I-EF.1.5 | Treatment window | 136 | 48 |
| I-GH.1.5 | Treatment window | 160 | 65 |
| I-IJ.1.5 | Treatment window | 167 | 105 |
| I-K.1.5 | Treatment window | 172 | 60 |
| I-L.1.5 | Treatment window | 110 | 67 |
| I-M.1.5 | Treatment window | 153 | 114 |
| 5-A.1.1 | Treatment window | 250 | 75 |
| 5-B.1.1 | Treatment window | 144 | 109 |
| PBGD-4 | Park adjacent to site | 76 | 9 |
| PGCD-5 | Park adjacent to site | nd | 10 |
| PBGD-6 | Park adjacent to site | 33 | 10 |

Block, Clark & Bishop made the following interpretation of the results:

"Many soils contain low level nonpetroleum hydrocarbon interferences. These interferences are presumed to be either naturally occurring humic materials or by-products of the petroleum hydrocarbon biodegradation process. The interferences are not effectively removed by the silica gel cleanup, but they do contain carbon hydrogen bonds. The presence of this interference falsely indicated that a healthy treatment process had stalled at some low to medium petroleum hydrocarbon level."¹⁴

In another paper by Block, Clark & Bishop, the following quote was found:

ONLY
C-H BONDS
DETECTED;
NOT ACTUALLY
PETROLEUM HYDROCARBONS, ONLY.

"Method 418.1 will measure any Freon-113 extractable, non-silica gel removable compound containing carbon hydrogen groups. This method does not provide any qualitative contaminant information other than the presence of the carbon hydrogen bond."¹⁵

Nyer and Skladany made the following statement:

"All materials (contaminants or benign materials) that are soluble in the solvent will be extracted. These materials may create positive or negative interferences with the hydrocarbon quantitation."²

Another factor to be considered is the possible interference of industrial materials or other contaminants. Many older urban/industrial areas contain significant amounts of fill materials which contain coal ash/cinders, asphalt, ash, decomposing lumber, etc. These materials will also generate high TPH values by Method 418.1 (Table 8.6). It can be stated that asphalt, as a petroleum based product, is accurate in showing positive TPH concentrations. There is a distinct difference, however, in the solubility, mobility, and regulatory classification of solid petroleum based products and liquid refined petroleum distillates.

Soil Matrix

Thomey, Bratberg, and Kalisz conducted a comparison of TPH in soil by 418.1 and GC/FID methods.¹⁶ They found fair agreement in sandy soils between 418.1 and GC/FID methods, but poor correlation with silt and clay soils. In addition, Thomey, Bratberg, and Kalisz theorized that colloidal and clay sized particles could remain in suspension in the Freon-113 extract, absorb infrared light, and cause a positive reading in the absence of petroleum hydrocarbons. The conclusions of the report stated:

"It is apparent that EPA Method 418.1 is not an appropriate technique for measuring TPH concentrations in certain types of soils. These types of soil can be categorized as weathered limestone, clays, and silts."¹⁶

Potter and Bruya also have reported false positives due to suspended solids (Figure 8.7).⁴ Some laboratories determine the IR absorbance at a fixed specific wavelength, therefore the analysts could not distinguish between a petroleum product and suspended clay particles.

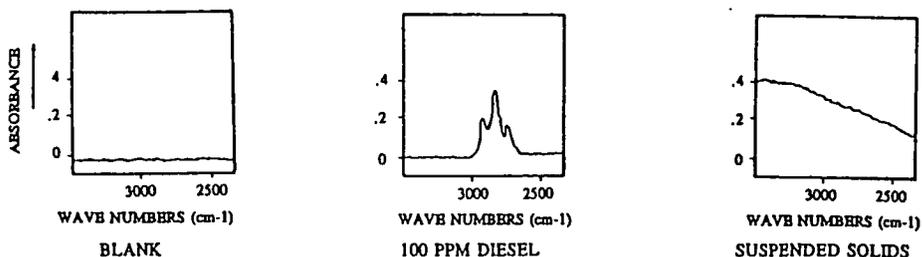


Figure 8.7. IR absorbance due to suspended solids⁴.

Alternative Methods

A full discussion of alternative methods to determine TPH concentrations in soil is beyond the scope of this chapter. GC methods are now widely used to determine TPH in soil.^{2,3,16-28}

The most commonly used technique is GC with flame ionization (FID) or photoionization detector (PID). Gas chromatography is based on a mixture separation of gas phase compounds (analytes) by the stationary phase (column). Different petroleum products will have different affinities for the stationary phase and, elute at different times. After separation in the column, the analytes are either burned by an FID or ionized by ultraviolet light in a PID. Quantification is by direct comparison of the sample with the same petroleum distillate fraction (i.e., gasoline contaminated soil with a gasoline standard).

The GC methods are usually divided into gasoline range (carbon range of C₆-C₁₀ and boiling point range of 60°C - 220°C) and diesel range (carbon range of C₁₀-C₂₈ and boiling point range 170°C - 430°C).²⁴

The gasoline range soil samples are analyzed by purge and trap with water or methanol as the purge fluid. The diesel range organics are extracted with a solvent (usually methylene chloride) followed by GC analysis.

There are several distinct advantages to GC methods. FIDs have similar responses for almost all petroleum hydrocarbons. A correlation can be made between elution time in the GC column and boiling points and carbon numbers of the sample.²⁶ If the type of petroleum fraction present in an environmental sample is unknown a fingerprint scan can be run to determine distillate type. A comparison is made directly between similar compounds (i.e., diesel to diesel) which helps to minimize the disparity between standards and samples.

Problems do exist with GC methods. As part of the quantification of petroleum distillates, an elution "window" is established for comparison. Due to the highly variable nature of petroleum products, a specific product may contain constituents that fall outside of this window. In turn, other compounds not intended to be quantified can elute in the same window. Heavy distillates (lubricating oils, residual fuels) are not easily separated or quantified by GC methods. In addition, industrial materials and soils with very high levels of organics may also test positive with the GC methods. The GC chromatograms by Iowa's OA-1 (gasoline range) and OA-2 (diesel range) for various petroleum products and organic materials are shown in Figure 8.8.

Although positive results were reported for the nonpetroleum organic materials by the GC/FID method, the "characteristics" of the chromatograms differ significantly from refined petroleum products. A significant departure from normal petroleum product chromatograms could signal the need for additional analytical work. These chromatograms should be compared to the IR spectra in Figure 8.6. The IR spectra offer no opportunity for identification of the material in question.

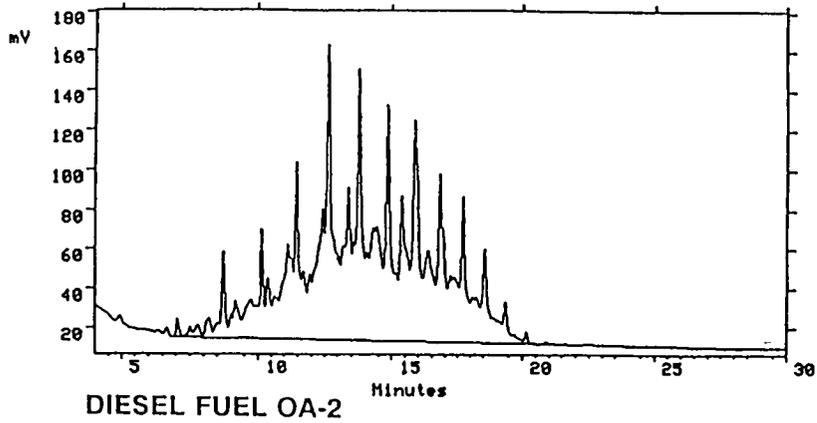
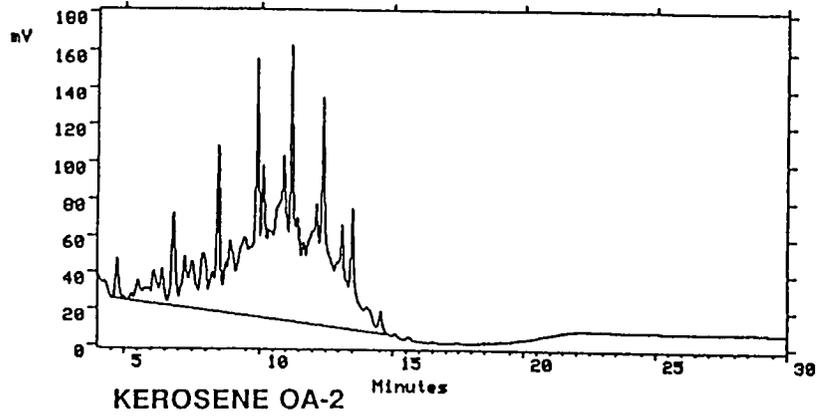
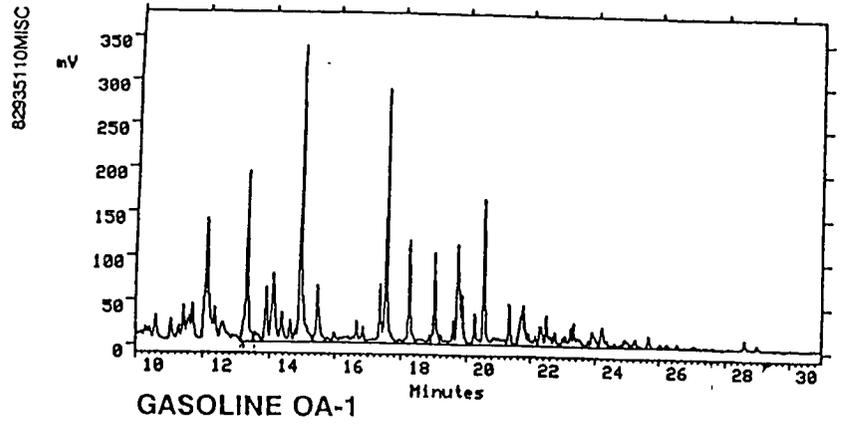


Figure 8.8.1. Gas chromatogram of various petroleum products and organic materials.

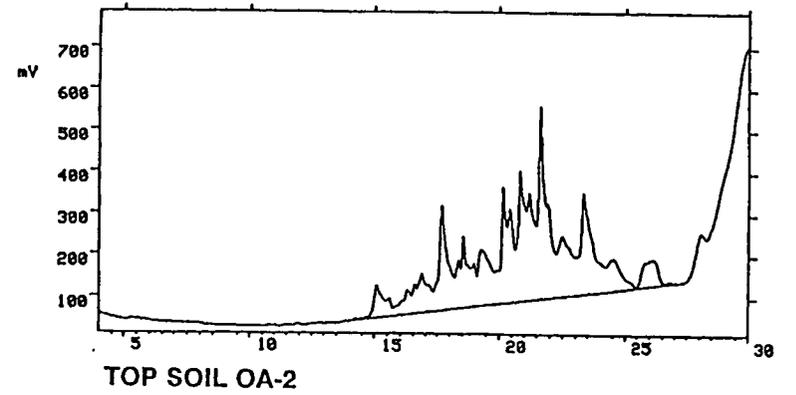
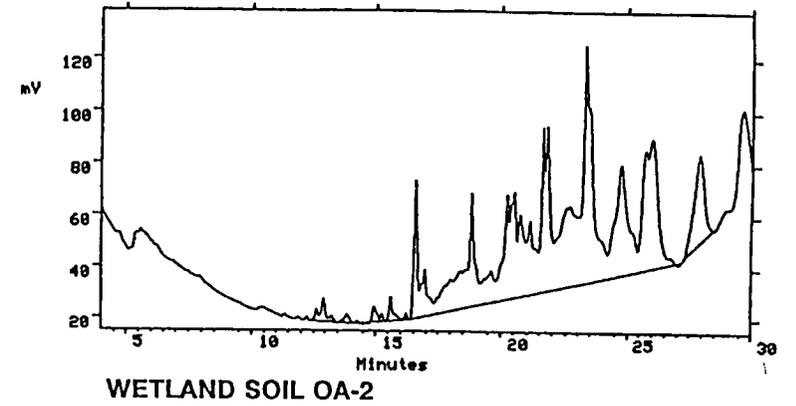
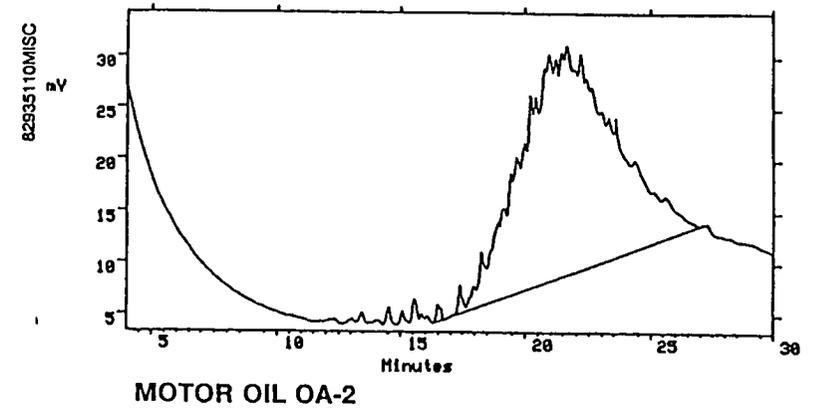


Figure 8.8.2. Gas chromatogram of various petroleum products and organic materials.

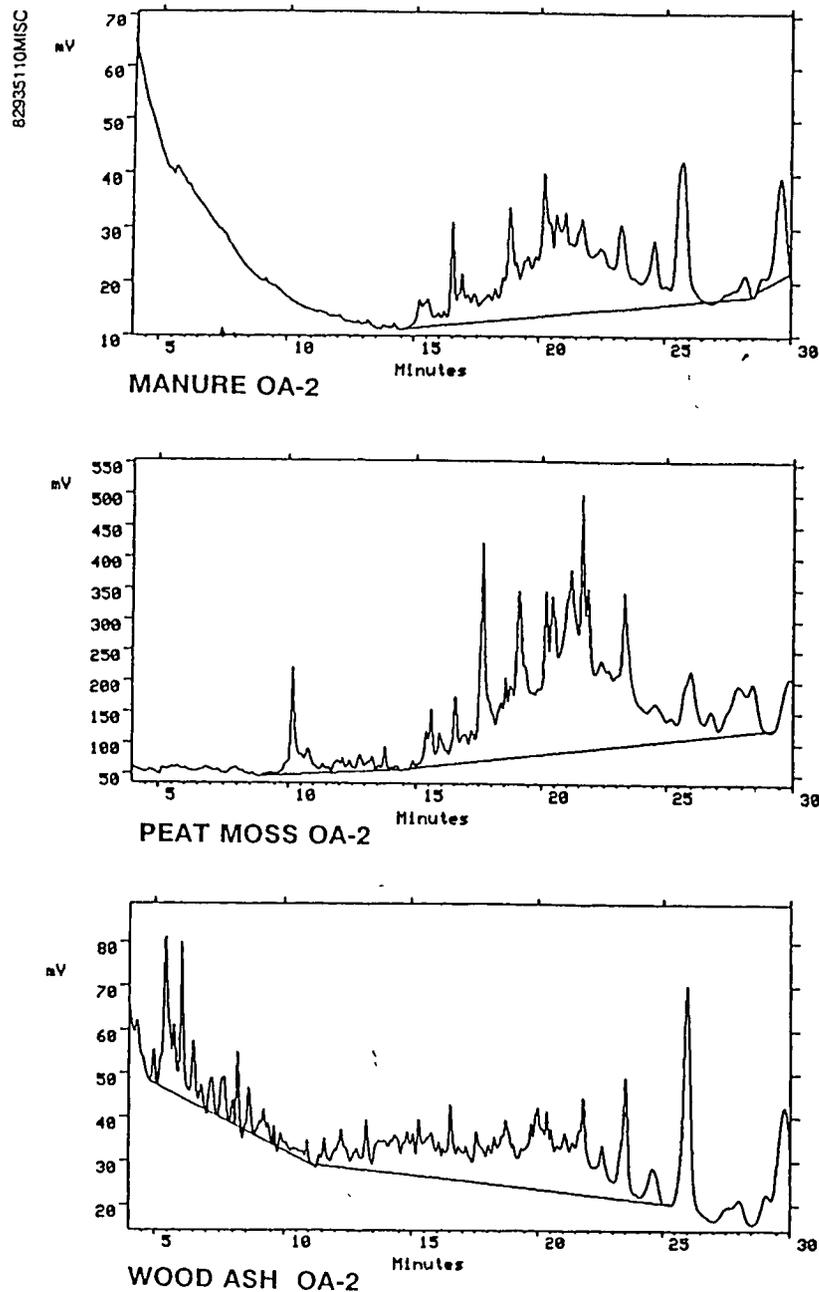


Figure 8.8.3. Gas chromatogram of various petroleum products and organic materials.

CONCLUSIONS

EPA Method 418.1 has been one of the most widely used procedures to determine TPH concentrations in soil. Studies performed by numerous groups have found the procedure to be prone to significant positive and negative biases. The key factors causing the biases are:

- Interlaboratory variations in analytical procedures;
- Negative bias due to volatilization of low boiling petroleum compounds;
- Negative bias due to poor extraction of high molecular weight hydrocarbons;
- Positive or negative bias due to disparity in absorption between the sample and the standard;
- Negative bias due to the removal of polar hydrocarbons in silica gel cleanup;
- Positive bias due to the measurement of naturally occurring organics or nonregulated petroleum based materials;
- Positive bias due to the suspension of clay particles in the Freon 113 extract; and
- Lack of petroleum type determination, preventing an accurate risk assessment.

The following statement appears in the definition section of Method 418.1:

"As in the case of oil and grease, the parameter of petroleum hydrocarbons is defined by the method. The measurement may be subject to interferences and the results should be evaluated accordingly."²⁹

The analysis of petroleum products in soil (as well as other analytes) is a complicated problem. The complex chemistry of petroleum products and the soil matrix make the development of an inexpensive, quick and accurate analytical procedure for TPH in soil almost impossible. Method 418.1 may be used for select site investigations, but the limitations and biases must be understood. Method 418.1 should not be used to assess soils affected by LBP petroleum products. Due to the high analytical variance, the procedure should not be used for remediation verification. The GC/FID procedures offer significant improvements in both quantification and the identification of interferences.

compounds. At this time, the GC methods appear to offer the best hope for standard TPH tests in soil and groundwater. The problems of heavy weight petroleum product quantification and the selection of suitable standards remain.

In addition to the problems which can be solved by the use of the more specific GC methods, a case can also be made that a solvent extraction method to determine TPH in soil has little relationship to the potential of the petroleum products to leach to groundwater, one of the principle exposure routes for petroleum releases. A more appropriate method may be a modified total characteristic leaching procedure (TCLP) or distilled water extraction method to determine leachability of the petroleum constituents.

ACKNOWLEDGEMENTS

The material in this chapter is a revision of material copyrighted by the National Groundwater Association, reprinted with their permission. The author wishes to thank Dr. Zwicker and Linda Stites of Environmental Science & Engineering, Inc. (ESE) for their assistance during the preparation and review of the manuscript; and also wishes to thank Jessica and Ellen George for their assistance in the collection of the samples.

REFERENCES

1. Oliver, T., and Kostecki, P., Ph.D., State-by-State Summary of Cleanup Standards, *Soils*, 1992.
2. Nyer, E.K. and Skladany, G.J., Relating the Physical and Chemical Properties of Petroleum Hydrocarbons to Soil and Aquifer Remediation, *Groundwater Monitoring Review*, Winter 1989.
3. Senn, R.J. and Johnson, M.S., Interpretation of gas chromatography data as a tool in subsurface hydrocarbon investigations, in *Petroleum Hydrocarbons and Organic Chemicals in Groundwater - Prevention, Detection, and Restoration*. 1985.
4. Potter, Thomas L. and Bruya, J., Analytical Techniques for Determining Petroleum Products in Soils, presented at the 7th Annual Conference on Hydrocarbon-Contaminated Soils, University of Massachusetts at Amherst. 1992.
5. Bergamini, T., Petroleum Product Chemistry and Analytical Tests for Petroleum Hydrocarbons, *Underground Tank Technology Update*, University of Wisconsin - Madison, April 1992.
6. Martin, Michael J., *Sonication Versus Soxhlet Extraction for Soil Analysis*, Environmental Lab., 1992.
7. Douglas, G.S.; McCarthy, K.J.; Dahlen, D.T.; Seavy, J.A.; Steinhauer, W.G.; Prince, R.C., and Elmendorf, D.L.; The use of hydrocarbon analyses for environmental assessment and remediation, in *Journal of Soil Contamination*, Vol. 1, No. 3, 1992.

8. EPA Method 418.1, total recoverable petroleum hydrocarbons by IR, *Groundwater Technical Analytical Bulletin*, Groundwater Analytical, Inc. Buzzards Bay, Maine, 1992.
9. Wingrove & Caret, *Organic Chemistry*, Harper & Row, 1981.
10. Solomons, T.W., *Organic Chemistry*, John Wiley & Sons, Inc., 1980.
11. Pouchert, C.J., *The Aldrich Library of FT-IR Spectra*, Edition 1.
12. Dragun, James, *The Soil Chemistry of Hazardous Materials*, Hazardous Materials Control Research Institute, Silver Spring, Maryland, 1988.
13. Tissot, B.P., Welte, D.H., Petroleum formation and occurrence, Springer Verlag, 1984 from Huc, A.Y., *Contribution a l'etude de l'humus marin de ses relations avec les Kerogenes*, thesis, Univ. Nancy, 1973.
14. Block, Clark, and Bishop, *Biological Treatment of Soils Contaminated Petroleum Hydrocarbons in Petroleum Contaminated Soils*, Volume 1990.
15. Block, Clark, and Bishop, Biological remediation of petroleum hydrocarbons, in *6th National Conference on Hazardous Wastes and Hazardous Materials*, 1989.
16. Thomey, Bratberg, and Kalisz, A comparison of methods for measuring total petroleum hydrocarbons in soil, in *NWWA/API Conference Petroleum Hydrocarbons and Organic Chemicals in Groundwater*, 1987.
17. American Petroleum Institute - 4449, *Manual of Sampling and Analytical Methods for Petroleum Hydrocarbons in Groundwater and Soil*, 1987.
18. Havlicek, Stephen C., *Characterization of Fuels and Fuel Spills*, Centric Coat Analytical Services, Inc., 1988.
19. Parr, J. L., Walters, G., Hoffman, M., Sampling and analysis of soils in the gasoline range organics in *West Coast Conference on Hydrocarbons Contaminated Soils and Groundwater*, 1990.
20. Walters, G., Zilis, K., Wessling, E.A., Hoffman, M., Analytical methods for petroleum hydrocarbons, in *1990 Superfund Proceedings, "Superfund 90"*, HMCRI, 1990.
21. Testa, S. M., Hydrocarbon product characterization: applications and techniques, *1990 Fourth National Outdoor Action Conference on Aquifer Restoration, Groundwater Monitoring and Geophysical Methods*, 1991.
22. Kostecki, P.T. and Calabrese, E.J., *Petroleum Contaminated Soils*, Lewis Publishers, Volume 2, 1989.
23. Kostecki, P.T. and Calabrese, E.J., *Petroleum Contaminated Soils*, Lewis Publishers, Volume 3, 1990.
24. Wisconsin Department of Natural Resources, *Leaking Underground Storage Tank Analytical Guidance*, April 1992.
25. Iowa Public Health & Environmental Laboratory-University Hygienic Laboratory-Methods OA-1 and OA-2.
26. ASTM: D 2887-84 - Boiling Range Distribution of Petroleum Fractions by Gas Chromatography.
27. ASTM: D 3328-90 - Comparison of Waterborne Petroleum Oils by Gas Chromatography.

↑ USE MODIFIED SPLP TO ASSESS LEACHABILITY.

28. Potter, Thomas L. 1989. Analysis of Petroleum Contaminated Soil and Water: An Overview, in Petroleum Contaminated Soils, Volume 2, Lewis Publishers, Inc.
29. Environmental Protection Agency, *Petroleum Hydrocarbons, Total Recoverable, Method 418.1 (Spectrophotometric, Infrared)*.