USE OF RISK-BASED STANDARDS FOR CLEANUP OF PETROLEUM CONTAMINATED SOIL

June 1994

AIR FORCE CENTER FOR ENVIRONMENTAL EXCELLENCE
ARMSTRONG LABORATORY
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DEPARTMENT OF THE AIR FORCE
HEADQUARTERS UNITED STATES AIR FORCE
WASHINGTON DC

MEMORANDUM FOR REMEDIAL PROJECT MANAGERS AND PROJECT TEAMS

SUBJECT: Use of Risk-based Standards for Cleanup of Petroleum Contaminated Soil

The Air Force has identified more than 4,500 sites which require environmental investigation and possible remediation. About 2,500 of these are contaminated with petroleum hydrocarbons such as jet fuel, diesel, gasoline, and heating oil. In order to responsibly and cost-effectively clean up these sites, valid standards must be established.

To ensure we protect human health and the environment, these standards must be based upon the risks posed by the various constituents of petroleum products. Many state and federal regulators, however, routinely enforce soil cleanup standards based on total petroleum hydrocarbons (TPH) levels ranging from 10 to 10,000 mg/kg. The TPH standard can be traced to the original California Leaking Underground Fuel Tank (LUFT) manual and/or research conducted by Stokman and Dime. It is clear from the aforementioned documents that the TPH standard was developed as a screening tool for compounds of regulatory concern, namely benzene, toluene, ethylbenzene, and xylenes (BTEX). However, these TPH screening standards were based on the incorrect assumption that the ratio of BTEX to TPH remains constant during natural weathering and active remediation. A review of data in the Installation Restoration Program Information Management System (IRPIMS), original bioventing research at Tyndall AFB, and data from the Air Force Bioventing Initiative clearly demonstrates that BTEX is preferentially removed over TPH by natural weathering and during active bioventing. Therefore, the TPH standard does not directly address the risks posed by the contaminants of major concern--namely the BTEX compounds.

This issue has been addressed by two Air Force agencies at Brooks AFB. The Air Force Center for Environmental Excellence (AFCEE) first questioned the TPH standard in a position paper found in the front of this document. Subsequently, the AFCEE sponsored an Air Force Institute of Technology (AFIT) Masters Thesis entitled "Evaluation of the Total Petroleum Hydrocarbon Standard for Cleanup of Petroleum Contaminated Sites" and the Armstrong Laboratory (AL) prepared a document entitled "Substitutions for Total Petroleum Hydrocarbons at JP-4 Contaminated Air Force Installations." These documents are herein provided and together provide valuable insight and tools for negotiation regarding the TPH/BTEX issue.

The attached materials not only provide the scientific justification regarding the fate, transport and toxicology of the true risk drivers, BTEX not TPH, but also show that most state regulatory agencies allow negotiation and acceptance of a risk-based BTEX cleanup standard. Indeed, several states have already moved away from the TPH standard in favor of benzene or BTEX, and it is our hope many more will follow. We believe that these documents will help bases and commands negotiate risk-based soil petroleum cleanup standards based on BTEX rather than continuing to use an inappropriate and costly TPH standard. Our goal is to clean up sites based upon health risks and we believe that soil cleanup standards based on benzene or BTEX concentrations accomplish this goal.

This publication is the result of a cooperative effort between AFCEE; AL; EA Engineering, Science, and Technology, Inc.; and AFIT students Captains Mark E. Smallwood and Rick A. Blaisdell. We invite your comments and suggestions. Please contact Lieutenant Colonel Ross N. Miller, AFCEE/ERT, 8001 Arnold Drive, Brooks AFB, TX, 78235-5357, DSN 240-4331, commercial (210) 536-4331.

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Using Risk-Based Standards Will Shorten Cleanup Time at Petroleum Contaminated Sites

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May 1992

USING RISK-BASED STANDARDS WILL SHORTEN CLEANUP TIME AT PETROLEUM CONTAMINATED SITES

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The Air Force has identified more than 4,500 sites that require environmental investigation and possible remediation. About 2,500 of these are contaminated with petroleum hydrocarbons such as jet fuel, diesel, gasoline, and heating oil.

Many of the sites that require remediation will be cleaned up based on an established regulatory standard. Many state and federal regulators routinely enforce a soil cleanup standard of 100 mg/kg total petroleum hydrocarbons (TPH). Several states have lowered this standard to 50 mg/kg TPH just for "good measure."

The 100 mg/kg TPH standard is often used across the board--without regard for the type of petroleum hydrocarbon contamination being remediated and with little thought about the risk-based standards on which that figure was established.

But where exactly did the number come from and and how did it become a standard in the first place? The answer can be traced to the California Leaking Underground Fuel Tank Field Manual, or LUFT, a manual designed to provide a consistent approach to underground storage tank spills (State of California, 1989).

The LUFT manual clearly illustrates that the 100 mg/kg TPH standard is based on a "medium" leaching potential of the soluble and toxic fraction of gasoline. The aromatic compounds of benzene, toluene, ethyl benzene, and xylene, known collectively as BTEX, form the most soluble and toxic fraction of fuel.

Different standards apply for diesel because the soluble and toxic fractions make up a lower percentage of the fuel. Also, the appropriate TPH standard changes for different leaching potentials.

It appears that TPH standards were originally developed as a screening tool by the California Department of Health Services (DHS). Using a logical and scientifically sound process, DHS started with state action levels for BTEX in groundwater. They are 0.7, 100, 680, and 620 parts per billion, respectively, and are based on the long-term health effects on a person drinking two quarts of water per day for 70 years.

After establishing acceptable groundwater standards for BTEX, a computer model, based on partitioning kinetics, was used to back-calculate the amount of BTEX in soil that could potentially produce the DHS action levels for BTEX in groundwater. This process was accomplished for low, medium, and high leaching scenarios.

Corresponding acceptable TPH concentrations in soil were approximated by using the calculated acceptable BTEX concentrations in soil divided by their percent of composition in gasoline or diesel. The resulting TPH and BTEX soil concentrations are summarized in Table 1. It is clear that the TPH standard is estimated from the theoretical risk-based standards for BTEX in soils that protect groundwater.

Table 1. Summary of Soil TPH and BTEX Standards (State of California, 1989)

	Leachability Potential		
	Low	**Medium**	**High**
Gasoline		**(mg/kg)**	
TPH	1,000	100	10
BTEX	1/50/50/50	.3/.3/1/1	(NA)
Diesel			
TPH	10,000	1,000	100
BTEX	1/50/50/50	.3/.3/1/1	(NA)

Although TPH is a good economical screening tool for assessing potential BTEX contamination, it makes more scientific sense to assess cleanup in terms of soil BTEX concentrations because our concern is with BTEX contamination of groundwater. More importantly, since there is little toxicological data for TPH, it is more protective of human health to assess cleanup in terms of BTEX for which volumes of human health data are available.

Remediation techniques such as soil vacuum extraction and bioventing have been shown to preferentially remove BTEX from soil at rates much faster than TPH removal. This occurs because these aromatic compounds (BTEX) are generally more volatile, soluble, and biodegradable than the large molecular weight aliphatic compounds that constitute the bulk of the fuel. In addition, at old weathered fuel spill sites, the BTEX may have naturally degraded to safe levels even though TPH concentrations remain high. Therefore, a soil cleanup standard based on BTEX, rather that TPH, will be more protective of human health while significantly reducing or potentially eliminating remediation costs at a given site.

Preferential removal of BTEX was recently demonstrated by a research project conducted at Tyndall AFB, FL (Miller et al., 1990). During the seven-month project , TPH concentrations were reduced by approximately one-third while BTEX was almost entirely removed. Figure 1 illustrates the results of average concentrations of seven specific compounds in soil before and after treatment. These numbers are based on 27 samples collected in a 20 m^3 test plot. It is obvious from Figure 1 that BTEX was preferentially removed over the longer chain compounds represented by n-decane through n-pentadecane.

The Air Force is currently investigating bioventing on a large scale to treat their petroleum contaminated sites. Based on a TPH standard of 100 mg/kg, it is estimated that remediation will take up to three years of site operation. However, past research (Miller, 1990) indicates that cleanup based on a risk-based BTEX standard could reduce remediation time to one year and save up to $100 million in unnecessary operation and maintenance costs. Although this cost savings is significant, increased protection of public health is the most important benefit of using a risk-based cleanup standard based on BTEX.

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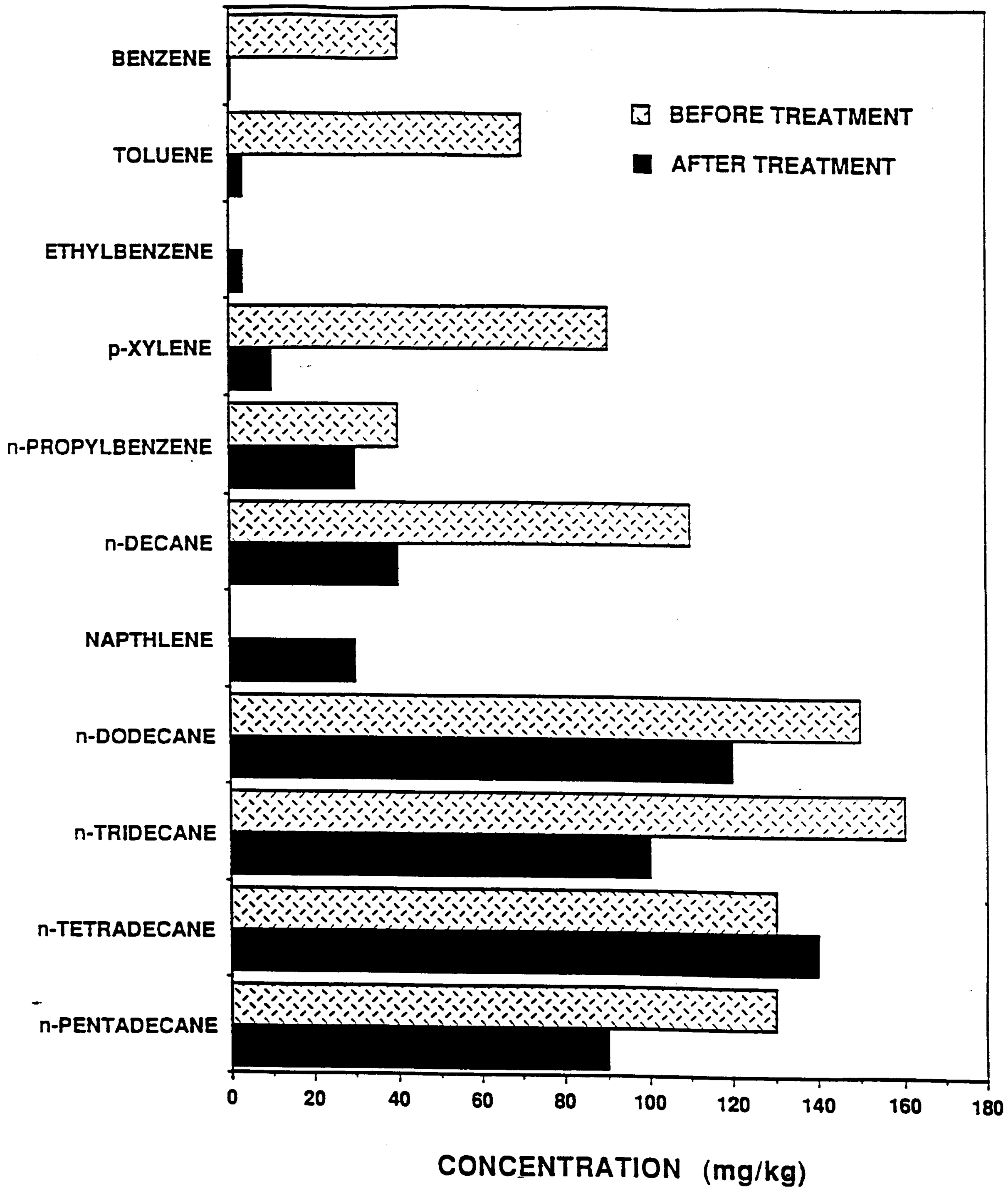

Figure 1. Average specific hydrocarbon concentrations before and after treatment in $20m^3$ test plot.

Evaluation of the Total Petroleum Hydrocarbon Standard for Cleanup of Petroleum Contaminated Sites

Thesis

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Presented to the Faculty of the School of Engineering
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September 1993

Acknowledgments

Many individuals contributed significantly to the successful completion of this thesis. The authors would like to express special thanks to Lt Col Michael Shelley, whose confidence in our ability to tackle this project and willing assistance when needed, made this an outstanding learning experience. We would also like to thank Lt Col Ross Miller, who inspired this work and provided valuable comments to make it better; Lt Col Mark Goltz, who expended time he really didn't have during a period of family crises to read this thesis and provide suggestions for improvements; AFCEE/ESD, Mr. Richard Anderson, and Mr. Corey Peshkey for their outstanding work in assembling IRPIMS data in a usable format; Mr. Paul Watkins for his computer programming help; Major Brian Woodruff for his guidance in statistics; and all of the many state regulators and technical experts who spent valuable time providing information through telephone interviews. Capt Blaisdell would like to give special thanks his wife, Jennifer, for her love, understanding, and support throughout the thesis effort and masters degree program. Lastly, both Capt Smallwood and Capt Blaisdell would like to thank their family and friends for their encouragement and inspiration in making this work possible.

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Abstract

This study evaluated the TPH (total petroleum hydrocarbon) cleanup standard for petroleum contaminated soils (PCS). Regulators from thirteen states were surveyed to characterize current standards used for PCS cleanup and regulatory viewpoints on the use of a TPH versus a BTEX (benzene, toluene, ethylbenzene, xylene) cleanup standard. BTEX was identified as the compound specific standard used most frequently by states for cleanup of PCS. The research found that the regulatory community considers BTEX the most mobile and toxic surrogates of petroleum. Regulators, however, expressed concern that the use of a compound specific standard, without an accompanying analysis for TPH, might result in residual soil contamination that may present risk.

This study also evaluated the ratio of BTEX to TPH in soil against the ratio found in a pre-spilled product. Based on JP-4 contaminated soil data contained in the Air Force Installation Restoration Program Information Management System database, this study demonstrated that the ratio of BTEX to TPH is statistically less than the pre-spilled product ratio. The results indicate that the assumption used by the California Leaking Underground Storage Tank manual and Stokman and Dime's research, that the ratio of BTEX to TPH remains constant in soil over time, is not valid. A conclusion is made that the use of this assumption in deriving TPH levels, which are protective of groundwater and human health, may be overly conservative. Lastly, this research identifies potential cost savings that would result if a BTEX based standard, versus a TPH based standard, were required at all Air Force petroleum contaminated sites. This study shows that only 13% of sites requiring cleanup under a TPH standard would require cleanup under a BTEX based standard.

EVALUATION OF THE TOTAL PETROLEUM HYDROCARBON STANDARD FOR CLEANUP OF PETROLEUM CONTAMINATED SITES

I. Introduction

General Issue

Out of the estimated three million underground storage tanks (UST) containing petroleum used throughout the country, as many as 500,000 may be leaking petroleum into the ground (13:83). The Environmental Protection Agency estimates that cleanup of contaminated soil and groundwater associated with these sites could cost as much as $32 billion (7:42). The Air Force estimates that sixty percent of its 4,000 hazardous waste sites are contaminated with petroleum hydrocarbons from aircraft fuel, gasoline, diesel fuel, or heating oil (34:53). According to Spain, petroleum contaminated soils represent the most pervasive hazardous waste cleanup problem faced by the U.S. Air Force (34:53).

RCRA Subtitle I provisions require the Environmental Protection Agency (EPA) to develop a comprehensive regulatory program for UST systems. From this requirement, the EPA has imposed technical standards for tank performance and management, and has identified corrective actions which tank owners or operators must take within 24 hours of a release (4:463). Soil contamination levels requiring cleanup, however, are delegated to the states. As a result, differing state standards now exist for cleanup of petroleum contaminated soils (3:75). Most states have set standards for TPH (total petroleum hydrocarbons), BTEX (benzene, toluene, ethyl benzene, and xylene), or a combination of TPH and BTEX.

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) was developed to provide funding and enforcement authority to clean up hazardous "waste sites" and to respond to hazardous waste spills (4:471). Although sites contaminated with spilled petroleum can be thought of as "hazardous waste sites", CERCLA specifically excludes petroleum and fractions of petroleum from its authority. Thus the Resource Conservation and Recovery Act (RCRA) is again the primary federal authority for requiring cleanup of petroleum releases to the environment (4:469).

According to Lieutenant Colonel Ross Miller, Chief of the Technology Transfer Division at the Air Force Center for Environmental Excellence (AFCEE), the TPH standard for soil cleanup can be traced to the California Leaking Underground Storage Tank (LUFT) manual. Miller has hypothesized that a compound specific standard, such as a BTEX standard, used in place of TPH, is a better measure of risk, would reduce cleanup requirements, and would save substantial taxpayer dollars.

Specific Problem

Because the Air Force must comply with all state standards in remediating hazardous waste sites, it has a vested interest in ensuring that an appropriate cleanup standard is used. In evaluating the appropriateness of pollution cleanup standards, there are many things that must be considered. Risk factors such as fate, transport, and toxicity of constituents, and monetary factors such as expected cost of remediation are but just a few of the considerations that must be addressed in such an endeavor.

This thesis evaluates, from a risk and cost perspective, the use of TPH as a cleanup standard for remediation of petroleum contaminated soils and compares the use of a TPH standard to a compound specific standard. This thesis also analyzes sampling and analysis data contained in the Installation Restoration Program Information Management System (IRPIMS) database to evaluate the use of the compounds upon which current state standards are based. The objective of this effort is to provide additional information to the scientific community concerning soil concentration levels of BTEX to TPH over time, and to provide support for or against the hypothesis that remediation to a TPH standard is more costly than remediation to a compound specific standard, such as a BTEX standard.

Objectives

The objectives of this thesis are as follows:

(1) characterize and explain current cleanup standards for soils contaminated with petroleum hydrocarbons,

(2) compare the use of the TPH standard with the BTEX standard.

(3) investigate how the relationship of BTEX to TPH in soil at sites contaminated with petroleum varies over time, and

(4) estimate potential cost savings to the Air Force that a non-TPH standard such as BTEX would create, if applied to sites currently regulated under a TPH standard, or combined BTEX/TPH standard.

Scope and Limitations

This thesis will focus on petroleum contaminated soil and associated cleanup standards. This thesis will not attempt to determine the soil regulations used in each specific state. Rather, an appropriate number of states will be sampled and a broad characterization made based upon this sample. Furthermore, the intent of this research is not to promote a BTEX based cleanup standard as the standard of choice for cleanup of petroleum contaminated soil. Rather, the intent is to evaluate the appropriateness of TPH as a cleanup standard and compare its application against the application of a BTEX standard.

II. Literature Review

Introduction

This literature review explores problems associated with sites contaminated with petroleum. First, general background information on petroleum is provided to give the reader an understanding of the complex makeup of this substance. Next, current analytical techniques used by laboratories to measure components of petroleum in soil and groundwater are discussed. A discussion on how individual states currently regulate cleanup of petroleum contaminated sites is then presented. This section includes a discussion of the use of TPH (total petroleum hydrocarbons) as a soil cleanup standard. In addition, criteria used in setting standards and information on state standards are also presented. The final section summarizes the literature on how petroleum contaminated sites present risk. This section includes a discussion on the use of both TPH and indicator compounds to measure risk to human health. In addition, properties of petroleum that effect its movement and concentration in soil and groundwater are identified here.

Petroleum Hydrocarbons

Petroleum can be defined as any hydrocarbon mixture of natural gas, condensate, or crude oil (26:23). Crude oil is the main source material for nearly all petroleum products. This material is distilled into a series of fractions to make different petroleum products; each characterized by the temperature and pressure of distillation. Thus, the type of petroleum product is a direct result of the boiling point of the crude used in the product. For instance, lighter fractions of crude with lower distillation temperatures are used for diesel, jet fuels, and light heating oils. Heavy fuel oils are made up of the residue from the distillation process and are composed of the heaviest fractions with the highest distillation temperatures. The temperature of distillation also functionally defines the volatility of the fuel, with gasoline's being highly volatile and residual fuels only slightly volatile (32:2).

Petroleum hydrocarbons are compounds of petroleum that consist almost entirely of the elements of hydrogen and carbon (26:23). They are not distinct entities, but rather, represent a continuum over a broad range, by molecular weight, of individual hydrocarbons. Gasoline, diesel fuel, and related products contain hundreds and sometimes thousands of different petroleum hydrocarbons (32:2). In addition to the process of distillation, the makeup of individual petroleum products is also dependent on refinery processes performed to give the product desired characteristics. For instance, gasoline's are created by blending different products of distillation with various additives in order to create a product that meets engine performance criteria. The significance of the production process is that some petroleum products may have little resemblance to the initial distillate produced during the initial processing of crude (32:2).

Petroleum hydrocarbons can be divided into four major structural groups. The first group is defined by chemists as alkanes (and by geologists as paraffin's). These hydrocarbons are saturated; which means that each carbon atom forms four single bonds with the hydrogen and other carbon atoms which make up each compound. These hydrocarbons are also aliphatic; which means that the carbon atoms are joined by straight or branched chain arrangements. This group usually dominates the gasoline fractions of crude oil. Examples of compounds in this group are hexane, heptane, octane, and decane. The second group is composed of cycloalkanes (or napthalenes). Hydrocarbons in this group are saturated hydrocarbons which are characterized by their ring type structure. Methlycyclo-pentane (C_6-H_{12}) and ethylcyclo-p-hexane (C_8H_{16}) are examples of hydrocarbons in this group. The third group is composed of the alkenes (or olefins). Hydrocarbons in this group are unsaturated, which means they contain at least two carbon atoms joined by more than one covalent bond, and aliphatic. The fourth group includes arenes (or aromatics). All compounds in this group contain at least one benzene ring. BTEX compounds fall into this group. Compounds in this group that contain three or more closed rings are termed "polynuclear" or "polycyclic" aromatic hydrocarbons (PAHs) (26:25-28).

Hartley and Ohanian provide one example of composition of unleaded gasoline. In their analysis, they found the following composition of hydrocarbons: 56% alkanes, 34% aromatics, 10% alkenes, and less than one percent PAHs (18-328).

The BTEX compounds of petroleum are of concern because of their toxicity (this is discussed further in the risk section of this chapter). Their makeup in gasoline, therefore, deserves some discussion here. Because of their distillation temperature, BTEXs are primarily found in the gasoline fraction of crude oil. They are also added to gasoline in the refining process. According to Baugh and Lovegreen, BTEXs have historically made up 15% to 25% of regular and unleaded gasoline's, and as high as 40% of premium gasoline's. BTEXs are usually found in lower concentrations in diesel fuels (6:148).

Measurement of Petroleum Hydrocarbons

To measure the amount of petroleum present in the soil or groundwater at a fuel contaminated site, either field screening techniques or laboratory analysis of samples is conducted. Because most states require laboratory analysis to measure compliance with standards, this section will focus on the laboratory methods used to identify and quantify petroleum compounds in soil and groundwater. This section also includes a discussion on the general analytical methods used to measure petroleum, the nature of the "total petroleum hydrocarbon" analysis, and the benefits and drawbacks of the analysis.

Analytical Methods. Several analytical methods are used to measure the components of petroleum hydrocarbons. The most commonly used method is EPA

Method 418.1, Total Recoverable Petroleum Hydrocarbons by Infrared Spectroscopy. As the name implies, this method is used to measure the total recoverable petroleum hydrocarbons. Because Method 418.1 does not accurately measure all of the fractions of petroleum, other analytical methods are used. EPA Methods 8020 and 8240 are commonly used to measure volatile hydrocarbons (7:47-48). Other methods which measure volatiles include Methods 602, 502, 502.2, 503.1, 524.1, and 624, or modification of these methods. Methods 610, 625, 8250, and 8270 are used to measure semi-volatile hydrocarbons. These methods are often used to measure the heavier fuel components that would be present in diesel fuel, kerosene, and #2 fuel oil (32:5).

Total Petroleum Hydrocarbon Analysis. As noted above, EPA Method 418.1 is the most commonly used method of measuring petroleum products in soil. This method is popular because it is relatively easy to perform, is inexpensive, and does not require extensive training of the analyst performing the method. The method offers excellent precision and reproducibility. The title also adds to its popularity. The title, "Total" Petroleum Hydrocarbons gives the impression, although false, that the method measures all hydrocarbon components of petroleum (5:45).

Method 418.1 does not measure all of the hydrocarbons present in petroleum. Rather, it measures the total concentration of a range of hydrocarbons. The method does not specify, therefore, the type of different hydrocarbon compounds measured (7:45). This is significant because the range of hydrocarbons present in a petroleum product can vary depending on the type of product and its age. Another limitation of the method is that it does not accurately measure the lighter fractions of gasoline. These fractions include benzene, toluene, ethyl benzene, and xylene (BTEX) compounds (7:46). Other limitations of measuring TPH are discussed in greater detail in the risk management section of this chapter.

According to Douglas and others, Method 418.1 should be used as a screening tool only. It is often applied, however, as an accurate analytical measurement without taking into account the method's limitations (15:198). The 418.1 method has the following sources of negative bias:

(1) poor extraction for high-molecular-weight hydrocarbons because of the use of freon in the extraction procedure,
(2) volatiles lost during the extract procedure,
(3) differences in the molar absorptivity between the calibration standard and product used,
(4) fractionation of soluble low-IR-absorbing aromatic hydrocarbons in groundwater during water washout,
(5) removal of 5- to 6-ring alkylated aromatics during the silica cleanup procedure, and
(6) preferential biodegradation of n-alkanes. (15:198-199)

Positive bias may be introduced from:

(1) product differences in molar absorptivity,
(2) partitioning from oil washout of soluble aromatics,
(3) naturally occurring saturated hydrocarbons, such as plant waxes present in the soil, and
(4) IR dispersion from clay particles (15:198-199).

Soil Cleanup Standards

As noted in Chapter I, the responsibility for establishing standards for cleanup of petroleum contaminated sites is delegated to the states under the Solid Waste Amendments of RCRA. This section provides information on rationale used by some of the states for developing their standards. This section also discusses studies which address levels of TPH in soil that (1) are protective of groundwater from excess BTEX concentrations, and (2) present a risk below one in a million. The results of a 1992 study on standards for cleanup of petroleum contaminated soil is summarized, problems with the state standards are discussed, and efforts to develop appropriate petroleum cleanup standards are presented.

Criteria for State Cleanup Standards. The standards and guidelines for petroleum contaminated soils were developed because of concerns associated with the leaching of hydrocarbon compounds to groundwater (7:43). According to Paustenbach and others, most states have set their guidelines for cleanup of petroleum contaminated soils in order to prevent contamination of groundwater and to protect human health (31:512). In many cases, however, regulators can not present either scientific basis or rationale behind the setting of their standards. For instance, some states have derived cleanup criteria in soils by using a multiple of the cleanup criteria used for groundwater. The Michigan soil standard for benzene, for example, was derived by multiplying the established groundwater standard by a factor of twenty (31:512). According to Heath and Atwood, "state regulators typically cannot provide technical justification for their soil TPH criteria" (19:12). Furthermore, "many regulators concede that soil TPH criteria in the range of 50 to 100 parts per million (ppm) probably originated as arbitrary values selected for specific sites" (19:12).

Soil TPH Levels Protective of Groundwater and Human Health. Some states refer to a study reported in the California Leaking Underground Fuel Tank (LUFT) manual as the basis for their soil cleanup standards (see Chapter V). California developed estimates of TPH soil concentrations designed to ensure that federal and/or state applicable or relevant and appropriate requirements (ARARs) for BTEX in groundwater are not exceeded. Other states reference studies conducted by Sofia K. Stokman and Richard Dime, both formerly of the New Jersey Department of Environmental Protection, as the basis for their cleanup standards. Stokman performed a study estimating concentrations of BTEX in groundwater migrating from soils containing petroleum hydrocarbons at a concentration of 100 ppm. Together, Stokman and Dime conducted a study which estimates the residual risk based on exposure to soils contaminated with 100 ppm TPH. These studies, in addition to the California LUFT manual work, are discussed below.

California Leaking Underground Fuel Tank (LUFT) Manual. The state of California developed the LUFT guidance to prescribe steps for categorizing sites contaminated with petroleum from leaking underground storage tanks. The manual applies to sites contaminated with either gasoline or diesel fuel and provides a rationale for using TPH analysis to measure risk associated with petroleum. According to the manual,

> [a]n analysis of Total Petroleum Hydrocarbons (TPH) should be included to check for other less mobile fuel constituents that could be adsorbed onto the soil in higher concentrations. This additional analysis may serve as a check for the possibility that BTX&E [BTEX] have migrated to deeper depths. (25:26)

Because benzene is volatile and soluble in water, it has a strong tendency to either evaporate or migrate to greater depths in the soil. If benzene is not present in the upper layers of soil at a site, it is possible that the substance might exist at greater depths (25:25). For this reason, TPH analysis is beneficial for identifying the presence of the less mobile components, which in turn, can indicate the possible presence of more mobile compounds elsewhere.

The LUFT manual provides guidance for levels of BTEX and TPH in soil which can safely be left in place without threatening groundwater (25:27). The manual states that acceptable TPH concentrations in soil were calculated by using state ARARs for BTEX in groundwater. A leaching potential analysis, using computer modeling, was used to derive acceptable levels of BTEX in soil from acceptable levels of BTEX in water. The model determines potential for leaching based on the following site characteristics: depth to ground water, subsurface fractures, precipitation, man-made conduits, and unique site features such as type of soil and location of public wells. Three categories of low, medium, and high leaching potential are developed. Acceptable TPH levels in soil are then approximated by using acceptable BTEX levels calculated for soil divided by their percent composition in gasoline or diesel (25:27).

In the calculation of acceptable TPH levels in soil, therefore, the study uses a virgin product ratio of BTEX to TPH. The use of a constant ratio of BTEX to TPH may not be valid because of preferential weathering or migration of BTEX. This assumption is challenged as part of this research effort.

Stokman Estimates of BTEX Constituents Migrating to Groundwater from Soils with 100 PPM TPH. According to Stokman, "[i]n order to develop an effective remedial program for soils contaminated with petroleum products, it is essential to define the ultimate fate of [the] toxic aromatic hydrocarbons in soil and ground water" (35:541). Stokman states that the BTEX constituents are considered the most toxic components of petroleum and are a threat to groundwater. Her research provides an estimate, based on computer modeling, of the concentrations of BTEX which would migrate to groundwater from soil remediated to 100 ppm TPH. Estimates are conducted for various types of petroleum, including leaded and unleaded gasoline, and No. 1 and No. 6 fuel oil (35:541).

In this research, Stokman first assumes that the ratio of BTEX to TPH, after the soil is remediated to 100 ppm TPH, is the same as the ratio which would exist in a product prior to spillage (35:543). Concentrations of BTEX in groundwater are then calculated by modeling the migration of these constituents through two different soil type scenarios (fine-sand soil and shaly-silt soil). Climate, soil, and groundwater estimates used in the models are worst case, and maximize the estimate of BTEX concentrations which would migrate to groundwater over a period of ten years (35:545). Biodegradation and volatilization of the BTEX are not considered in the analysis.

Stokman's results indicate that a 100 ppm TPH soil cleanup objective for petroleum results in maximum groundwater concentrations of BTEX below USEPA limits identified in ARARs. Stokman recommends that,

> "[a]n alternative [to] remediating the soil to 100 ppm of total PHs [TPH] is to let the cleanup objective be determined by the most hazardous constituent in a particular petroleum product. For example, benzene could be the cleanup criterion

> for soils contaminated with low boiling fractions of petroleum containing significant concentrations of benzene..." (35:555)

Stokman and Dime Estimate of Residual Risks from Petroleum Contaminated Soils. Stokman and Dime, in this research, compare soil cleanup levels for carcinogenic constituents of petroleum (including benzene) to a 100 ppm TPH cleanup objective (36:342).

In this study, the authors present risk assessment and soil cleanup objectives for individual chemical constituents which "have the highest toxicity, the ability to migrate, and/or are present in significant amounts" (36:342). They state that benzene is of primary concern in lighter fuels such as gasoline, and carcinogenic polycyclic aromatic hydrocarbons (CaPAHs) are of primary concern in certain heavy residual oils (36:342-343).

In their analysis, Stokman and Dime estimate the residual soil concentrations of carcinogenic constituents when 100 ppm TPH is used as a cleanup objective. They make an assumption that the ratio of CaPAHs and benzene to TPH, after the soil is remediated to 100 ppm TPH, is the same as that from the pre-spilled product (36:344). The authors explain that the migration of contaminants to groundwater is of concern, but their study is concerned primarily with chronic effects due to long term exposure to contaminated soils (36:343). The results of their study show that a soil cleanup objective of 100 ppm TPH from gasoline, fuel oil, fresh motor oil, or lubricating oil "appears to result in residual soil levels of CaPAHs and benzene not exceeding a 1×10^{-6} cancer risk" (36:345).

Current State Cleanup Standards. A study conducted in August, 1992 by the Association for the Environmental Health of Soils (hereafter referred to as the "Soils magazine study") presents information on the standards currently used by states for cleanup of petroleum contaminated soils (29:14-24). The study reports for each state: (1) the type of petroleum product regulated, (2) the analytical parameters and laboratory tests required to measure each product, (3) notification level, (4) action level, and (5) recommended cleanup levels for each product.

Although the study reports recommended cleanup levels for almost every state, the study does not distinguish whether these levels are strictly enforced. According to Heath and Atwood however, standards used by the states are guidelines, recommendations, or suggestions, rather than laws (29:12). According to Bell and others, "only a few of the states have set definitive standards or corrective action levels" (8:79). Bell and others also suggest that states that do have set levels often provide an alternative methodology for establishing site-specific cleanup levels based on risk. In addition, they state that almost all of the states allow for modification of the standards as the situation demands (8:79,89).

It is clearly evident from the Soils magazine study that standards used for soil cleanup are inconsistent from state to state. They are thus very difficult to compare. The standards vary by (1) type of product regulated, (2) chemical indicators used to measure each product, (3) laboratory protocols used to quantify the amount of each compound, and (4) cleanup levels set. These are discussed in greater detail below.

First, the petroleum products regulated in each state are different. The majority of the states regulate only two petroleum products: gasoline and diesel. Other states, however, regulate other petroleum products such as: kerosene, jet fuel, heavy oil, fuel, oil, waste oil, mineral spirits, Naphtha, motor fuel, oils, and heating oils. Thus, an initial evaluation of petroleum products regulated shows that there is little consistency in the products regulated by different states.

Second, the Soils magazine study also shows that compounds used to measure a type of petroleum product varies from state to state. For example, states require analysis for one or more of the following compounds: TPH, benzene, toluene, ethyl benzene, xylene, 1,2- dibromomethane, PAH, naphthalene, MTBE and others. In general, most states require both TPH and BTEX analysis to measure gasoline. These states may or may not have standards for other components in addition to TPH and BTEX. Another inconsistency is that some states do not require analysis for all of the BTEX components. Kansas, for example, requires that gasoline contamination be measured by TPH, benzene, and 1,2-dichloroethane.

The study also shows that in quite a few states, different laboratory test protocols are required by different states for measuring the same component of petroleum. For example, the following methods are used by different states for measuring concentrations of BTEX: Methods 602, 624, 8020, 8240, 8340, 5030, 8260, 8021, or modifications of these methods.

Finally, the same inconsistency exists in notification levels, action levels, and cleanup levels. The recommended TPH cleanup levels for gasoline generally range from non-detectable or background (Maryland), to 10,000 parts per million (California). Recommended cleanup levels for BTEX are overall much lower, with standards set in the parts per billion range.

According to Bell and others, the lack of a consistent approach can be attributed to several causes. First, limited guidance has been provided to the states for establishing soil cleanup standards at the federal level, particularly from the EPA. Second, there is a lack of agreement on the appropriate analytical methods for measuring contaminant concentrations in the soils. Third, each petroleum contaminated site is different and has specific hydrogeological properties that effect the fate and transport of spilled product (8:77).

Heath and Atwood note that a trend may be developing towards site-specific guidelines, rather than set standards. They note that several states that had submitted set cleanup levels during a 1991 survey of state regulations, submitted "site specific" target levels for 1992 (19:12). They explain that this indicates regulators in some states, rather than using set standards, are attempting to integrate soil risk assessment into the remediation decision-making process (29:22).

The literature identifies several other problems in the way state standards are set. First, the basis or rationale for cleanup levels used by the states have not been clearly identified. Second, the standards sometimes vary between agencies within the same state. Third, the levels of cleanup set by each state are often set in a haphazard rather than scientific and systematic manner (31:512).

The way many of the standards are set "often results in excessively costly remediation and monitoring requirements" (19:22). These costs can be significant, affecting both the regulated community and society as a whole (31:512). For instance, according to Jernigan and others, a three-fold decrease in cleanup levels (which is insignificant to most regulatory considerations) can result in a ten-fold increase in cleanup costs (23:11-12). Furthermore, the standards are overly conservative. According to Heath and Stanley:

> Petroleum sites are being remediated to policy based standards that are orders of magnitude more conservative than the human health, risk based standards applied at Superfund sites and RCRA Corrective Action sites. This inequity would seem to represent a misallocation of scarce resources that could be more effectively applied elsewhere. (19:12)

<u>Efforts to Standardize Petroleum Cleanup Standards</u>. According to Daugherty, petroleum contamination from underground storage tanks is an on-going problem of regulatory concern. This is due to the scientific uncertainty associated with predicting the environmental fate and transport of petroleum. This uncertainty will continue to make the establishment of a health-based soil cleanup standard a difficult and controversial process (12:55,57). Bauman also recognizes lack of scientific understanding of the fate and transport of petroleum, and states that additional research is needed in this area. Research

needs include "assessment of the relationship (if any) between TPH values and mobility of specific contaminants" (7:46).

Risk Associated with Petroleum Contaminated Sites

Risk assessment is a quantitative evaluation of hazards posed by exposure to a toxicant. The goal of a risk assessment is to estimate the probability of adverse effects on humans, domestic animals, wildlife, or ecological systems from exposure to a chemical or physical agent (28:5). To determine the amount of risk presented by petroleum contaminated soils, one must evaluate information on the toxicity, environmental fate and transport, and exposure pathways of its constituents (27:284).

This section provides an overview of risk associated with petroleum to human health, and summarizes the literature on indicators of risk to human health. First, information on (1) the use of a total petroleum hydrocarbon standard to assess risk, (2) the use of indicator compounds to assess risk, and (3) the use of BTEX as an indicator compound is presented. Second, fate and transport mechanisms that effect the concentration of petroleum in soil, and effect a constituent's mobility in the subsurface are identified. Lastly, possible exposure pathways which may exist for contaminated soils are listed.

Overview of Risk Potential. As stated previously, in order to ascertain the risk to human health from soils contaminated with petroleum it is necessary to understand the health effects, persistence and mobility, and possible routes of exposure for the constituents in petroleum. The toxicity of a chemical refers to the degree it is poisonous or harmful. Persistence and mobility refer to a chemical's staying power and ability to move through a pathway to a receptor. Pathways are routes which petroleum constituents can take to reach receptors (10:374).

Use of "TPH" to Measure Risk. As mentioned briefly in the analytical methods section, TPH analysis is not an appropriate measure of risk (7:45-46). Because of the inherent variability in the TPH analysis methods, it is currently not possible to directly relate potential health risks with concentrations of TPH. For instance, Method 418.1 cannot be used to distinguish between different petroleum products, and thereby determine the relative mobility or toxicity of various petroleum product. When using TPH analysis methods, for example, there is no easy way to say if 300 ppm of "TPH" measured at one site will represent the same level of risk as 300 ppm TPH from another site (7:45-46).

This is significant because different petroleum products vary in composition, and the composition of a product is affected by the age of the product. Bauman gives a hypothetical example that highlights a limitation of the TPH analysis. He states that if Method 418.1 is used to measure gasoline at a spill site where the product was freshly spilled, the petroleum might be composed of hydrocarbons in the range of C_6 through C_{12}. At an older site, where the same fuel had weathered, however, hydrocarbons in the C_8 through C_{12} range would probably be present. He explains that because TPH analysis does not distinguish between the different hydrocarbons, the analysis cannot be used to accurately compare risk between the two sites (7:45-46).

Use of Indicator Compounds to Assess Risk. A widely used and accepted approach for measuring risk associated with petroleum is to identify and measure indicator compounds (10:12; 9:43; 9:22; 11:380). The use of indicator compounds is based upon two assumptions. The first assumption is that the toxicity of the indicator compound(s) represents the toxicity of the mixture. The second assumption is that the mobility of the indicator compound(s) represents the mobility of the mixture. Constituents in the subsurface that exhibit little or no mobility pose little risk because there is little potential of reaching a receptor (11:380; 9:22).

The use of indicator compounds is extremely attractive because of the large number of compounds that make up petroleum. Measuring and evaluating the risk of a product containing over one thousand compounds would be time consuming and very impractical (17:253). According to Jernigan and others, when considering health-based cleanup levels, one or two key compounds will usually represent the majority of the risk. They estimate that 75%-90% of the risk from petroleum is associated with these key compounds (23:17). According to Gilbert and Calabrese, the compounds selected as indicators should ideally be the most toxic, present in the highest concentration, the most mobile, and the most persistent in the environment (17:253).

BTEX as an Indicator Compound. Because indicator compounds are usually defined as those that are the most toxic and mobile in soil and groundwater, many states focus on the use of BTEX in their state standards and/or guidelines (9:45). Furthermore, BTEX components are selected by the EPA as indicator compounds for No.2 fuel oil in the Petroleum, Underground Storage Tank, Risk Assessment Procedures Manual. EPA's reason is the BTEXs have relatively higher toxicity and water solubility than the other petroleum constituents (17:267). Benzene in particular is a known carcinogen and "is responsible for a significant fraction of potential health risks at petroleum-contaminated sites" (15:274).

Other Indicator Compounds. Some studies note the existence of compounds in petroleum that are not used as indicator compounds, yet have the potential to present substantial risk. One such chemical is benzo(a)pyrene. Benzo(a)pyrene is a polycyclic aromatic hydrocarbon that is linked to cancer, though it has a lower mobility potential than BTEX (26:31). Another chemical identified is methyl tert-butyl ether (MTBE), which is a common additive to gasoline (32:6). Bell and others note that MTBE is perceived to be relatively toxic and is therefore a potential risk agent (32:6).

Fate and Transport. The fate of petroleum after it is leaked into the subsurface is important in identifying potential pathways to human receptors. According to Daugherty, transport mechanisms that affect dissolved contaminants in groundwater include advection, dispersion, and diffusion (12:29). The most significant transformation process for organic chemicals is bacterial biodegradation (12:29). According to Denahan and others, chemical and physical properties also effect the fate and transport of petroleum in soil. These properties include the nature of the specific constituent, the age of the constituent, and hydrogeological parameters of the site (13:29).

Constituent Properties. According to Frankenberger, the environmental fate and transport of petroleum constituents is dictated largely by the compound's physical and chemical properties (16:254). He states that the five most significant chemical and physical properties affecting dissolved petroleum concentrations include:

(1) water solubility
(2) organic carbon coefficient (Koc)
(3) vapor pressure
(4) Henry's law constant
(5) octanol/water coefficient (Kow)

According to Wilson and Brown, the distribution of petroleum contamination in the subsurface is also a function of the geochemical characteristics of the soil formation (37:173). These characteristics include pH, conductivity, and organic mass.

Age of Spill. The age of a spill also affects the concentration levels of petroleum in the subsurface. According to Denahan and others, there are three fate mechanisms affecting sorbed contaminant concentrations. These mechanisms include volatilization, dissolution and leaching, and biodegradation (13:102). According to Frankenberger, biodegradation and volatilization tend to selectively remove the lighter chain hydrocarbons such as benzene, toluene, and xylenes over the heavier components of petroleum (16:254).

Exposure Pathways. Hartley and Ohanian identify five exposure pathways which characterize how petroleum from a contaminated site may reach humans. These exposure pathways include: (1) ingestion of contaminated groundwater, (2) ingestion of contaminated soil, (3) dermal contact with contaminated groundwater (4) dermal contact with contaminated soil, and (5) inhalation of volatilized hydrocarbons (18:328).

Conclusion

The literature review indicates that TPH analysis can be used as adequate means of screening for petroleum at petroleum contaminated sites. There is agreement in the literature, however, that TPH analysis cannot be used to adequately assess the risk to human health from petroleum. The literature seems to support the use of indicator compounds, such as BTEX, for measuring the specific components that present risk. Caution is required, however, to ensure that chemicals other than the indicator compounds measured, do not remain in the soil and present risk. MTBE is an example of such a compound.

A review of the existing information on soil cleanup standards for petroleum shows that the standards are inconsistent from state to state. The literature review raises the following concerns with regards to standards. First, the standards for soil lack appropriate technical justification. Second, state regulators are unaware of how their soil remediation standards were developed. Third, the standards are overly conservative, causing a misallocation of public and private resources. And finally, it is unclear whether state regulators currently enforce the recommended cleanup levels noted in the Soils magazine study (such as a standard of TPH criteria of 100 ppm). Although two authors report that the "recommended cleanup levels" set by many states are guidance levels rather than required standards, these authors did not quantify a number or percentage of states to which this applies. Additional research is needed in this area.

III. Methodology

Overview

To meet the research objectives, a combination of methodologies was used. First, the literature is reviewed and evaluated to determine the current use of TPH and BTEX by the states. Second, telephone interviews are conducted to obtain technical opinions on the use of TPH versus a compound specific standard. State regulatory personnel, and civilian and Air Force technical experts in the area of petroleum contaminated soils were interviewed. Third, the researchers analyzed sampling and analysis data from Air Force petroleum contaminated sites to evaluate the relationship between TPH and BTEX over time. Fourth, an estimate of the number of Air Force sites that would not require cleanup under a BTEX cleanup standard is conducted to evaluate cost savings which would result if a BTEX standard were applied.

Literature review

The literature presents some explanations for how and why current cleanup standards were developed by individual states. The researchers found, however, that the literature does not 1) fully characterize the use of the TPH standard versus the use of a compound specific standard, (2) fully characterize the flexibility states allow for cleanup of petroleum, and (3) explain the extent to which risk assessments are used by the states.

Analysis of State Standards

The literature review identifies the cleanup standards for cleanup of petroleum contaminated soil. Although studies have been conducted which report the cleanup standards used for petroleum, no in-depth analysis of the standards is available in the literature. The researchers conducted an analysis of state standards reported in the December 1992 issue of Soils magazine to fill this need (19).

This analysis further characterizes the current cleanup standards for petroleum contaminated soils by (1) categorizing types of petroleum used by each state, (2) evaluating the basis for each state's standards (TPH, BTEX, or both), and (3) assessing other chemical compounds used in state standards. An analysis of the gasoline and JP-4 standards is also performed to identify the highest, lowest, median, and most frequent recommended cleanup levels used for cleanup. The results of this analysis are presented in Chapter IV.

Interviews with State Regulators and Technical Experts

The researchers used interviews with state regulators and technical experts as a second approach to characterizing and explaining the cleanup standards currently used for cleanup of petroleum contaminated soils. These interviews also provide information for comparing the use of a TPH standard against a BTEX standard. Although all state regulators could be considered "technical experts" in their field, "experts" will hereafter be used in this paper to refer to the other professionals interviewed who are not state regulators.

The interviews were non-scheduled and semi-structured, with the information gathering the main objective of each interview. In order to obtain accurate viewpoints of interviewees, the researchers prompted the interviewees to clarify their responses and to provide additional information, when appropriate. A semi-structured interview format was selected for this study because the researchers believed that this type of format would elicit the most information in the time allowed.

State Regulators. A stratified random approach was selected to establish the sample of state regulators in order to obtain technical opinions from state regulators in states that have different soil cleanup regulations. First, states were separated into groups, based on the type of standard used by each state. Three groups were established: (1)

states with standards based on TPH, (2) states with standards based on BTEX, and (3) states with standards based upon both TPH and BTEX. The December 1992 Soils magazine provided the information necessary to establish these groupings. Four states from each group were then randomly selected. An additional state from the TPH/BTEX group was selected to make a sample of twenty-five percent of the states. Lastly, the researchers used the state regulator referenced in Soils magazine as points of contact for the selected states.

The researchers developed an initial survey questionnaire and conducted several interviews. After interviewing an initial sample of regulators, the researchers revised the questionnaire. The initial questionnaire was changed to (1) include additional questions, (2) change existing questions to elicit better responses, and (3) to delete unnecessary questions. After the questionnaire was revised, the researchers re-contacted the regulators initially interviewed to obtain their responses to added questions.
The final survey questionnaire was formulated to obtain the following information:

(1) Difference between standards and guidelines
(2) Flexibility in the state standards
(3) Whether risk assessments are required or allowed
(4) Whether TPH levels are considered in assessing risk
(5) How states regulate soil contaminated with jet fuel
(6) Whether site age makes a difference in how a petroleum contaminated site is regulated
(7) Technical basis for the states standards
(8) References to California LUFT manual or NJ's Stokman and Dime study
(9) Regulatory opinions on the advantages and disadvantages of a TPH standard
(10) Regulatory opinion on the appropriateness of different cleanup levels for different petroleum products
(11) Regulatory opinion on the advantages and disadvantages of a compound specific standard
(12) Regulatory opinion on the chemical compounds that should be used as indicators of TPH contamination

Limitations to Survey of State Regulators. Because of the type of survey and the methodology employed, several limitations exist that affect the utility of the survey results. These limitations are discussed below.

First, the sample consists of state regulators responsible for enforcing state cleanup standards for petroleum contaminated soil and groundwater. Although each regulator's position and experience gives credibility to their response, one cannot assume that the regulators' responses are representative of their state's official position. Furthermore, because responses to the survey questionnaire often require the regulators to provide both interpretations of their state's standards and technical opinions, different regulators in the same state may have provided different responses to the same question. Similarly, because of the inconsistencies that exist in petroleum cleanup standards from state to state, one cannot assume that this survey captured all regulatory approaches.

Finally, there are other limitations and biases that require discussion. These limitations exist due to the structure of the survey questionnaire, the nature of the interviews conducted, and the type of data collected.

First, bias may exist due to the wording of the survey questionnaire. Some of the questions contained in the questionnaire may have prompted more frequent responses. For instance, when the researchers asked the interviewees to provide advantages and disadvantages of a TPH cleanup standard, they also asked them to comment on risk and mobility considerations. These considerations are therefore addressed more frequently.

A second bias may exist from the nature of the semi-structured interview process used. In an attempt to obtain more information, the researchers may have asked questions to prompt more in-depth responses. The result of this bias is that more complete responses may have been provided by some interviewees because of prompting conducted by the researchers.

A third limitation is the qualitative nature of the responses and context through which they were provided. Interviewees were not prompted to give an exhaustive explanation of their knowledge, nor were they asked to identify information in which they feel is most important. In addition, it was necessary to make some interpretations of the interviewees responses to categorize each response. These limitations are important in interpreting the responses on advantages and disadvantages of a TPH and compound specific standard. One cannot assume that those interviewed agree or disagree with the advantages and disadvantages provided by other interviewees. Nor can one assume that the responses provided by the interviewees are those they feel are most important.

Although these limitations exist and should be kept in mind when reviewing the results provided, many useful conclusions can be drawn from the collected information. An indication of regulatory concerns and viewpoints on issues associated with the use of a TPH verses a compound specific cleanup standard is provided. Furthermore, the survey provides valuable insight into the standards currently used for cleanup of petroleum contaminated soils and into the technical opinions of regulators enforcing cleanup.

Technical Experts. The sample of technical experts included members of the Council for the Health and Environmental Safety of Soils (CHESS), an organization established to produce a generic method for deriving soil cleanup levels, and an Air Force technical expert working petroleum contaminated soil issues. These two groups were selected because of their members' expertise in the field of petroleum contaminated soil.

The researchers established a survey questionnaire for the technical experts which contained many of the same questions asked of the state regulators. This questionnaire included additional questions to obtain technical opinions on (1) the importance of risk assessment in developing cleanup standards for petroleum contaminated soils, (2) risk assessment criteria which are important for establishing a soil cleanup standard, and (3) whether strict TPH level are appropriate for cleanup of petroleum contaminated soil.

Evaluation of Survey Responses. The results of all interviews were analyzed to both characterize the application of cleanup standards by each state and the interviewees' technical perspectives on cleanup standards for petroleum contaminated soils. For each question, an attempt was made to characterize and categorize each response, to determine the most frequent responses, and to rank the responses by frequency. The researchers then analyzed significance of the responses.

Relationship of BTEX to TPH

As established in the literature review, many states reference studies which calculate the levels of TPH that can be left in the soil. The studies (1) estimated groundwater BTEX concentrations that would result from soils contaminated at 100 ppm TPH, and (2) evaluated the cancer potential of exposure to soils contaminated at 100 ppm TPH. An assumption used in these studies, however, is that the relationship of BTEX to TPH remains constant over time. Associated with evaluating the use of the TPH standard (the overall goal of this research), the researchers hypothesize that this assumption is overly-conservative and may not be valid for petroleum contaminated soils. It is, therefore, necessary to investigate how the relationship of BTEX to TPH in petroleum contaminated soil varies over time.

The methodology selected by the researchers for this objective is an analysis of Air Force sampling and analysis data for sites contaminated with petroleum. Through an analysis of this data, the researchers tested the hypothesis that BTEX is preferentially weathered over TPH with time. Subsequently, this would show that the relationship between BTEX and TPH is not constant and that the assumptions used in the studies referenced in the literature review are not valid.

The researchers used information contained in the Installation Restoration Program Information Management System (IRPIMS) for this research. IRPIMS contains sampling and analysis data for Air Force contaminated sites which have been investigated for cleanup under the Installation Restoration Program (IRP). Because Air Force petroleum contaminated sites are investigated under the IRP, IRPIMS contains extensive sampling information on petroleum sites. The database is maintained by the Air Force Center for Environmental Excellence (AFCEE) at Brooks AFB, Texas.

AFCEE estimates that 60% of all sampling and analysis information collected under the IRP has been entered into IRPIMS. AFCEE is in the process of entering the other 40%, which currently exists in hard copy technical reports, into IRPIMS. This study, therefore, was conducted using only the sampling information contained in IRPIMS and does not incorporate other sampling information which has not been entered.

To obtain information on sites contaminated with petroleum, the researchers requested information for all sites in which samples for both BTEX and TPH had been taken. The specific fields requested and believed necessary to analyze the relationship of BTEX to TPH are shown in Table 1. This table identifies the field parameter name in IRPIMS, explains the information the field represents, and provides a description of how this information would be used. Hydrogeological data was also requested and the field descriptions are provided in Table 2. The researchers asked AFCEE to download all information from IRPIMS into a format which could be used by a database program on a personal computer.

The researchers requested that AFCEE download only specific analytical data necessary for this research. This included analytical data for benzene, toluene, ethylbenzene, total xylenes (o-, m-, and p-), and TPH concentrations. AFCEE standardized the results of these analyses in milligrams of contaminant per kilogram of soil (parts per

TABLE 1

DESCRIPTION OF IRPIMS DATA FIELDS REQUESTED

Field Name*	Definition	Purpose
AFIID	Air Force Installation Identification	To differentiate sites by Air Force installation, plant, or base
SITEID	Site Identification	To correlate samples from the same site at different time periods
SITENAME	Site Name	To correlate samples from the same site at different time periods
LOCID	Location Identification (typically synonymous with monitoring well ID, borehole ID, etc.)	To correlate BTEX and TPH concentrations from the same location for ratio calculations
NCOORD	North State Plane Coordinate (the North-South distance in feet from the an installation reference location)	To correlate samples from the same site at different time periods in the event no Site Name provided
ECOORD	East North State Plane Coordinate (the East-West distance in feet from the an installation reference location)	Needed to correlate samples from the same site at different time periods in the event no Site Name provided
LOGDATE	Log Date (date the sample was taken)	To correlate samples for TPH and BTEX over time
MATRIX	Sampling Matrix (soil, groundwater, etc.)	To verify sample measured from soil matrix
SBD	Sample Beginning Depth	To correlate BTEX and TPH concentrations from the same depth for ratio calculations
ANMCODE	Analytical Method Code (ex. TPH typically E418.1)	To sort data by analytical method if necessary
PARVQ	Parameter Value Qualifier (equal to: "=", non-detect: "ND", trace: "TR"	To categorize samples (sample concentrations with a PARVQ of "TR" considered zero for this analysis because detection below the LABDL for that PARVAL)
PARVAL	Parameter Value (sample concentration for BZ, TOL, EBZ, XYL, and TPH)**	Needed for ratio calculations (units standardized in ppm by request)
LABDL	Laboratory Detection Limit (provided for each sample PARVAL)	To remove PARVALs below LABDL (all PARVALs below LABDL considered non-detects for this analysis

*These field names are identified in the <u>IRPIMS Data Loading Handbook</u>.

** "BZ" = benzene, "TOL" = Toluene, "EBZ" = ethyl-benzene, "XYL" = xylene

TABLE 2

DESCRIPTION OF HYDROGEOLOGICAL DATA REQUESTED

Field Name*	Definition	Purpose
LITHCODE	Lithology Classification Code (general classification of soil type: sand, gravel, clay, etc.)	To correlate BTEX to TPH ratios with type of soil over time
STRATCODE	Stratigraphic Order (soil layer type identifier)	Additional information about site soil layers that may be needed
ASTMCODE	ASTM Soil Classification (specific classification of soil type)	To correlate BTEX to TPH ratios with type of soil over time
PARVAL (pH, specific conductance)	Parameter Value (soil pH and specific conductance for each TPH or BTEX sample	To assess BTEX to TPH ratios over by pH and specific conductance
LABDL	Laboratory Detection Limit (obtained for each PARVAL field)	Needed as a check of PARVALs
UTMCODE	Units of Measure (pH units, specific conductance units)	Needed if pH or specific conductance used in analysis

*These field names are identified in the IRPIMS Data Loading Handbook.

million). Analytical data for pH, temperature, and specific conductance was also requested.

Relationship of BTEX to TPH Over Time with Varying Hydrogeological Site Conditions. This relationship was not determined due to IRPIMS data limitations (see Chapter VI for detailed explanation). A description of the intended methodology, however, is provided here.

The intended methodology compares the relationship of BTEX to TPH for two or more samples taken at the same location at different points in time. This comparison determines whether or not the weathering rate of BTEX constituents over time is statistically different from the weathering rate of total petroleum hydrocarbons. This comparison also addresses hydrogeological site conditions to determine if the rate is influenced by soil type. An assumption is made that the contamination sampled at the earlier date would represent the same soil sampled at later dates.

The time which transpired between sampling intervals is used to plot relative decreases in the ratio of BTEX to TPH over time for multiple samples. From this information a correlation in the rate of product degradation over time could be calculated. Further plots are developed to assess BTEX to TPH ratios for varying hydrogeological site conditions. Precipitation rates, hydraulic conductivity, soil type, and sample depth are examples of different site conditions.

<u>Ratio of BTEX to TPH in Soil</u>. The methodology used to evaluate this ratio compares the BTEX to TPH ratios calculated from petroleum site data contained in IRPIMS to the same ratio calculated from information about the specific petroleum product provided in the literature. An assumption is made that the initial spill (time zero) ratio of BTEX to TPH in the soil medium is the same as the pre-spilled product ratio. Short term separation which might result from different soil absorption/desorption properties of either BTEX or TPH is not considered in this analysis.

The researchers first grouped the IRPIMS data by type of petroleum. Sorting of the data was required to separate out unusable information. Information in which the type of contamination could not be identified in the site name field, was considered unusable. The researchers then calculated a ratio of BTEX to TPH for all samples which had TPH and BTEX present above the laboratory detection limit. Although more than one actual sample may have been taken to report these results, a "sample" will be defined here as all results reported for the same (1) date, (2) sampling location, and (3) sampling depth.

The researchers then calculated an average ratio of BTEX to TPH present in a virgin petroleum product. An assumption is made here that this ratio is representative of the petroleum in its pre-spilled state. The calculated ratios from IRPIMS were then compared to this virgin product ratio. This was performed to challenge the validity of assumptions used in the California LUFT study and in Stokman and Dime's research: that the relationship of BTEX to TPH remains constant in soil over time. The Wilcoxin

Signed-Rank Test was used to determine if the ratio of BTEX to TPH for the actual field samples declines statistically from the calculated virgin product ratio.

From this analysis, the researchers provided evidence that the BTEX components of petroleum weather faster than the longer chained hydrocarbons measured by TPH. This shows preferential removal of BTEX over TPH with time.

Evaluation of Potential Cost Savings

To determine if a potential for cost savings would result if a BTEX standard was applied to all Air Force petroleum contaminated sites, the researchers compared the number of petroleum sites (in IRPIMS) that would require cleanup under a BTEX based standard to the number of sites that would require cleanup under a TPH based standard.

To determine the BTEX and TPH levels used as the basis for categorizing a site to be cleaned up, the researchers chose the cleanup levels cited most often by all fifty states. These cleanup levels, therefore, represent the mode of the cleanup levels currently used by the states. The identified petroleum sites were then characterized by level of contamination. For example, if a site contained at least one sample with contamination above the mode BTEX cleanup level, it was assumed to require cleanup. The same is true for the TPH samples at the petroleum sites.

From this characterization, the percentage of sites requiring cleanup under the mode BTEX cleanup standard and the percentage of sites requiring cleanup under the mode TPH cleanup standard was determined. These percentages are used to predict cost savings potential. Even though the IRPIMS database does not contain sample information from every Air Force site, the researchers consider these percentages to be representative of Air Force petroleum contaminated sites.

Summary

The methodologies outlined in this chapter will provide support for answering the research objectives. This information, in turn, will provide the data and information necessary for the researchers to make conclusions on the validity and effectiveness of the TPH cleanup standard as compared to a non-TPH standard such as a BTEX standard.

IV. Analysis of State Standards

This section provides an analysis of the standards used for cleanup of petroleum contaminated soils, as reported in the December 1992 issue of Soils Magazine. This analysis (1) examines the categories of petroleum regulated by the states, (2) reviews the cleanup standards for each category and examines the chemical indicators other than TPH and BTEX used, (3) examines the number of states which base their standards on TPH, compound specific, or both TPH and compound specific cleanup levels, and (4) characterizes the range of TPH and BTEX cleanup levels used by the states. The purpose of this work is to characterize the state standards. From the results, conclusions can be made on the current applications of TPH and compound specific standards.

Categories of Petroleum Regulated

Most states report petroleum cleanup guidelines for two basic categories of petroleum products: gasoline and diesel. Only six states report cleanup guidelines for petroleum products other than gasoline or diesel. The other categories of petroleum include: waste oil, fuel oil, and crude oil.

Two states place either kerosene or jet fuel in the same category as gasoline. Fifteen states, however, categorize other middle distillate fuels with diesel. These products include: heavy oil, weathered gas, jet fuel, kerosene, heating fuel, illuminating oils, naphtha, and mineral spirits. Because gasoline and diesel are the two major categories of petroleum regulated by the states, the following analysis focuses on these products.

Gasoline Cleanup Requirements

A summary of recommended cleanup levels for sites contaminated with gasoline is provided in Table 3. Several items on this table are worth noting. First, twenty-two

TABLE 3

SUMMARY OF GASOLINE CLEANUP LEVELS (ppm)

State	SS(2)	TPH	BTEX	Benzene	Toluene	EB	Xylene	Others(3)
Alabama		100		0.005	2	0.7	10	XXX
Alaska		50	10	0.1				
Arizona		50		0.13	200	68	44	
Arkansas	X	100	10					
California	X	10-10,000		.3-1	.3-50	1-50	1-50	XXX
Colorado		100-500	20-100					
Connecticut (1)								
Delaware	X	100	10					
Florida	X							Field SCR
Georgia		100-500	20-100					
Hawaii				.05-1.7	10-21	1.4-7		
Idaho		40-200						
Illinois			11.705	0.005				
Indiana	X	20						
Iowa		100						
Kansas		100		1.4				XXX
Kentucky			1					
Louisiana	X	*	*					
Maine	X							Field SCR
Maryland		0-100	0					XXX
Massachusetts(1)								
Michigan				0.0014	0.016	0.0014	0.006	
Minnesota	X	50-100	40					XXX
Mississippi		100	100					
Missouri		50-500	2	.5-2	1-10	2-50	2-50	
Montana		100	10	1				
Nebraska	X	*		*	*			
Nevada		100						
New Hampshire		10	1					
New Jersey				1	500	100	10	
New Mexico			100	10				XXX
New York				24	20,000	8,000	200,000	XXX
North Carolina(1)								
North Dakota		100						
Ohio	X	*		*				
Oklahoma	X	50		0.5	40	15	200	
Oregon	X	40-130						
Pennsylvania	X	10		0.01	0.02	0.02	0.07	XXX
Rhode Island	X	300						XXX
South Carolina	X	*	*					
South Dakota	X	10-100		*	*	*	*	XXX
Tennessee	X	100-1000	10-500					
Texas		100	30					
Utah	X	30-300		.2/1	100-900	70-600	1000-10000	XXX
Vermont	X	20	*					
Virginia	X	*	*					
Washington	X	100		0.5	40	20	20	
West Virginia	X	100	10					
Wisconsin (1)		10						
Wyoming (1)		30-100						

(1) Standards being revised

(2) Site specific provisions for cleanup

(3) See Table 4 for list of compounds

* Parameters Used (Site Specific Cleanup)

states report site specific provisions for cleanup. This means that these states incorporate site specific factors in establishing site cleanup requirements. Single asterisks indicate the chemicals a state uses in their cleanup standards, but for which no cleanup levels are established. Second, many states report a range of cleanup values, rather than a single recommended cleanup value. Third, four states are revising their standards. Lastly, ten states have recommended cleanup levels for specific compounds other than TPH and BTEX. The compounds used in addition to TPH and BTEX for gasoline are listed in Table 4.

Table 4 shows that, for the most part, there is little consistency in compounds other than BTEX and TPH used by the states. Lead and methyl tert-butyl ether (MTBE) are the only compounds that occur with any frequency. Each analysis is required by four states. Halogenated volatile organics (HVOs) and volatile organic compounds (VOAs) are included in this table because these analyses differ from the commonly cited analyses for BTEX compounds, used by other states.

Diesel Cleanup Requirements

A summary of the cleanup levels used for diesel by the states is reported in Table 5. A list of compounds used in addition to TPH and BTEX for regulation of diesel are listed in Table 6. This table reflects that there is also little consistency in chemical compounds used other than BTEX and TPH to indicate diesel contamination. Some consistency is shown in the use of polynuclear aromatic hydrocarbons by five states and naphthalene, also by five states.

Basis for Soil Cleanup Standards

Table 7 summarizes the basis for soil cleanup standards used for gasoline and diesel. This table identifies for each state whether their standards are based on TPH, specific compounds, or both TPH and specific compounds. A column for BTEX is

TABLE 4

COMPOUNDS OTHER THAN TPH/BTEX USED FOR GASOLINE

Compound	AL	CA	KS	MD	MN	NM	NY	PA	RI	SD	UT
1,2 Dibromomethane	X										
1,2 Dichloroethane			X								
Heavy Metals								X			
HVOs		X									
Lead	X							X		X	X
MTBE				X	X		X			X	
Naphthalene							X				X
Polynuclear Aromatic Hydrocarbons											
VOAs						X			X		
BTEX	X	X	X	X		X	X			X	X
TPH	X	X		X					X	X	X

included for gasoline because several states have cleanup levels for BTEX alone (without TPH or other specific compounds). On the other hand, no states have BTEX only standards for diesel.

Table 7 shows that nine states have cleanup standards based on TPH alone for gasoline and twenty-one states for diesel. This is significant because these states do not use any other compound indicators, including BTEX, for assessing cleanup requirements for contaminated sites.

Table 7 also shows that five states have a cleanup standard based on BTEX alone for gasoline and seven states have a compound specific cleanup standard, without requirements for TPH, for gasoline. Five states have a compound specific cleanup standard for diesel. These findings are significant because they identify that states use compound specific standards for gasoline and diesel.

TABLE 5

SUMMARY OF DIESEL CLEANUP LEVELS (ppm)

State	SS(2)	TPH	BTEX	Benzene	Toluene	Ethyl B.	Xylene	Other(3)
Alabama		100		0.005	2	0.7	10	XXX
Alaska		100						
Arizona		100						
Arkansas	X	100						
California	X	100-10,000		0.3-1	0.3-50	1-50	1-50	
Colorado		100-500	20-100					
Connecticut(1)								
Delaware	X	1000						
Florida	X							FIELD SCR
Georgia	X	100-500	20-100					
Hawaii				0.5-1.7	10-20	1.4-7		XXX
Idaho		100						
Illinois			11.705	0.005				XXX
Indiana	X	20						
Iowa		100						
Kansas		100		1.4				XXX
Kentucky								XXX
Louisiana	X	*						
Maine	X							FIELD SCR
Maryland		0-100	0					XXX
Massachusetts(1)								
Michigan		100		0.02	0.016	0.0014	0.006	XXX
Minnesota	X	50-100	10					
Mississippi		100	100					
Missouri		50/500	2	0.5-2	1-10	2-50	2-50	
Montana		100						
Nebraska	X	*		*	*			
Nevada		100						
New Hampshire		10	1					
New Jersey				1	500	100	10	
New Mexico		100						
New York				24	20,000	8,000	200,000	XXX
North Carolina(1)								
North Dakota		100						
Ohio	X	*	*					XXX
Oklahoma	X	50		0.5	40	15	200	
Oregon	X	100-1,000						XXX
Pennsylvania	X							
Rhode Island	X	300						
South Carolina	X	*	*					XXX
South Dakota	X	10-100						
Tennessee	X	100-1,000	10-500					
Texas		100	30					
Utah	X	100-500		0.2-1	100-900	70-600	1000-10000	XXX
Vermont	X	10						
Virginia	X	*	*					
Washington	X	200						
West Virginia	X	100						XXX
Wisconsin(1)		10						XXX
Wyoming(1)		30-100						

(1) Standards being Revised
(2) Site Specific Provisions for Cleanup
(3) See Table 6 for list of compounds

* Parameters Used (Site Specific Cleanup)

TABLE 6

COMPOUNDS OTHER THAN TPH/BTEX FOR DIESEL

	AL	HI	IL	KS	KY	MD	MI	NY	OH	OR	SC	UT	WI	WV
Aromatic Hydrocarbons									X					
Acenaphthene		X	X					X						
Anthracene			X					X						
Benzo(a)anthracene								X						
Benzo(a)pyrene		X						X						
Benzo(b)fluroanthene								X						
Benzo(g,h,i)perylene								X						
Benzo(k)fluroanthene								X						
Chrysene								X						
Dibenz(a,h)anthracene								X						
1,2, Dibromomethane	X													
1,2 Dichloroethane				X										
Fluoranthene		X	X					X						
Fluorene			X					X						
Halogenated Volatile Organics										X				
Indeno(1,2,3-cd)pyrene								X						
MTBE						X								
Naphthalene		X	X					X			X	X		
Phenanthrene								X						
Polynuclear Aromatic Hydrocarbons	X				X		X						X	X
Pyrene			X					X						
Total Carcinogenic PNAs			X											
Total Non-Carcinogenic PNAs			X											
BTEX	X	X	X	X[1]		X	X	X	X		X	X		
TPH	X	X		X		X	X		X		X	X	X	

(1) Benzene Only

Finally, note that two states (FL, ME) use field screening for cleanup determinations. These states are significant because they do not require a laboratory analysis of soil samples for making cleanup determinations.

Range of Cleanup Levels for Gasoline

Table 8 reports an analysis of the recommended cleanup levels reported in Soils magazine for TPH and BTEX for gasoline. The low, high, median, and mode values used are reported here. This information will be used in Chapter V for analysis of Air Force

TABLE 7

BASIS FOR SOIL CLEANUP STANDARDS

	Gasoline				Diesel			Field
State	TPH	BTEX	Both(2)	Other(3)	TPH	C.S.	Both	SCR
Alabama			X	X			X	
Alaska			X		X			
Arizona			X		X			
Arkansas			X		X			
California			X	X			X	
Colorado			X				X	
Connecticut (1)								
Delaware			X		X			
Florida								X
Georgia			X				X	
Hawaii		X				X		
Idaho	X				X			
Illinois		X				X		
Indiana	X				X			
Iowa	X				X			
Kansas			X	X			X	
Kentucky		X				X		
Louisiana			X		X			
Maine								X
Maryland			X	X			X	
Massachusetts (1)								
Michigan		X					X	
Minnesota			X	X			X	
Mississippi			X				X	
Missouri			X				X	
Montana			X		X			
Nebraska			X				X	
Nevada	X				X			
New Hampshire			X				X	
New Jersey		X				X		
New Mexico		X		X	X			
New York		X		X		X		
North Carolina (1)								
North Dakota	X				X			
Ohio			X				X	
Oklahoma			X				X	
Oregon	X				X			
Pennsylvania			X	X				
Rhode Island	X			X	X			
South Carolina			X				X	
South Dakota			X	X	X			
Tennessee			X				X	
Texas			X				X	
Utah			X	X			X	
Vermont			X		X			
Virginia			X				X	
Washington			X		X			
West Virginia			X				X	
Wisconsin (1)	X						X	
Wyoming	X				X			
Total	9	7	29	11	18	5	21	2

(1) Standards being Revised
(2) Standards Based on TPH plus BTEX or Others
(3) Standards Based on Compounds other than TPH or BTEX

TABLE 8

COMPOUNDS USED IN GASOLINE STANDARDS (ppm)

Compound	Low	High	Median	Mode
TPH	0	10,000	100	100
BTEX	1	100	10	10
Benzene	0.0014	24	0.5	1
Ethyl Benzene	0.0014	9,000	20.5	50
Toluene	0.016	20,000	40	40
Xylene	0.006	200,000	32	50

cost savings if a BTEX standard where adopted for cleanup of Air Force petroleum contaminated sites.

Worth noting is that Maryland has the strictest standards for TPH, with recommended cleanup to background or non-detectable levels. California has the highest levels, set at 10,000 ppm TPH. Furthermore, the most commonly cited cleanup level for TPH is 100 ppm. Seventeen states use 100 ppm TPH in their standards as a recommended cleanup level. It appears that many states also use a multiple of this standard. Five states have recommended cleanup levels of 50 ppm TPH, and four states have recommended levels of 10 ppm TPH.

Conclusions

This chapter characterizes the standards used for cleanup of petroleum contaminated soil. From the information presented above, one can clearly see the wide variation that exists in the cleanup standards used by the states. This chapter presents several significant findings:

(1) State standards exist for two major categories of petroleum, gasoline and diesel.

(2) TPH and BTEX are the predominant indicators used for measuring the amount of petroleum present in petroleum contaminated soil.

(3) Several states are committed to the use of a compound specific based standard. Five states have a gasoline cleanup standard based on BTEX, and seven states have a diesel cleanup standard based on specific compounds.

(4) More states are committed to the use of a TPH based standard. Nine states have a gasoline cleanup standard based on TPH, and twenty-one states have a diesel standard based on TPH.

(5) States use chemical indicators other than BTEX and TPH for indicating the presence of petroleum contaminated soil. For states that do not feel comfortable using a BTEX only standard, these chemicals provide a starting point for compounds other than BTEX which might be considered for a compound specific standard.

(6) The most commonly cited standard for cleanup of petroleum is 100 ppm TPH.

In summary, although TPH is the most commonly used standard for cleanup of petroleum contaminated soils, this analysis shows that a compound specific standard is both used and accepted by several states.

V. State Regulator and Technical Expert Interviews

As discussed in Chapter 3, a sample of state regulators and technical experts were interviewed to characterize and explain the current cleanup standards for soils contaminated with petroleum hydrocarbons. After the researchers began the interviewing phase of this research, it became apparent that the state regulators were able to provide the critical information needed to evaluate the use of TPH as a cleanup standard. The researchers found the regulators to be the most knowledgeable about both the rationale for the establishment of petroleum cleanup standards, and about technical considerations important in the development of a cleanup standard. For this reason, the originally planned methodology was altered slightly to focus on interviewing state regulators.

This chapter is divided into four sections. The first two sections provide a description of state regulators and technical experts interviewed. The third section forms the basis for this chapter and reports the findings from the state regulator and expert interviews. Lastly, the fourth section provides information obtained from questions which were posed to the experts and not asked of the state regulators.

State Regulator Interviews

Regulators from twenty-five percent of the states were interviewed. A list of these regulators is provided in Table 9. The abbreviation of the state each regulator represents will be used to identify the regulator who provided information during the survey.

Changes to Regulator Survey Questionnaire After completing six interviews, the researchers changed the original survey questionnaire to incorporate better and more specific questions. Questions were added to determine (1) whether states have flexible cleanup standards, (2) whether TPH levels are considered in assessing risk, (3) how jet fuel contaminated soil is regulated, and (4) whether states used the California LUFT

TABLE 9

STATE REGULATORS INTERVIEWED

State	Abbreviation	Name	Telephone
Delaware	DE	Pat Ellis	(302) 323-4588
Illinois	IL	Tom Hornshaw	(217) 782-6762
Kentucky	KY	Doyle Mills	(502) 564-6716
North Dakota	ND	Mark Mittelsteadt/Martin Schock/ Gary Berreth	(701) 221-5166
New Mexico	NM	Keith Fox	(505) 841-9478
New York	NY	Frank Peduto	(518) 457-9412
Pennsylvania	PA	Doug Cordelli	(717) 657-4080
Rhode Island	RI	Michael Mulhare	(401) 277-2234
Texas	TX	Chris Chandler	(512) 908-2245
Virginia	VI	Dave Chance	(804) 527-5188
Washington	WA	Lynn Coleman	(206) 438-3073
Wisconsin	WI	Laurie Egre	(608) 267-7560
Wyoming	WY	LeRoy Feusner/ Shawn Sullivan	(305) 777-7096

manual or New Jersey's Stokman and Dime research in establishing their cleanup standards.

The phrasing of several questions was also changed in order to elicit more in-depth responses. Phrases such as "why or why not?" and "if so, when?" were added to several questions. Finally, the researchers found that several questions did not provide any useful information. These questions were deleted from the questionnaire.

After the questionnaire was revised, the researchers re-contacted the regulators initially interviewed to obtain their responses to added questions.

Technical Expert Interviews

Four technical experts in the area of petroleum contaminated soil were interviewed. Three experts are members of the Council for the Health and Environmental Safety of Soils (CHESS), and one expert is a member of the United States Air Force. These individuals were interviewed because the researchers believed that their technical opinions might add a different perspective to questions asked of the state regulators. All four are well known in the field of petroleum contaminated soil, and several have published journal articles or books in this area. These experts are listed in Table 10.

TABLE 10

TECHNICAL EXPERTS INTERVIEWED

Name	Position	Telephone
Dr. Bruce Bauman	Senior Environmental Scientist American Petroleum Institute (API)	(202) 682-8000
Dr. Paul Kostecki	Research Associate Professor University of Massachusetts at Amherst Managing Director for CHESS	(413) 545-4610
Lt Col Ross Miller, Ph.D.	Chief, Technology Transfer Division Air Force Center for Environmental Excellence (AFCEE)	(210) 536-4331
Dr. Thomas Potter	Director of the Mass Spectrometry Facility (UMASS at Amherst)	(413) 545-3505

Interview Findings and Discussion.

Information gathered during the interviews with state regulators and technical experts is summarized and discussed below. Note that questions about specific standards used by each state were not asked of the technical experts. Additional technical questions posed to the experts are reported in the section which follows.

Title and Agency of Interviewees. The name of each regulator was obtained from the Soils magazine survey. If the regulator listed in the survey was not available, another regulator in the agency was contacted. All individuals interviewed work for agencies responsible for cleanup of petroleum contaminated soil, and are completely knowledgeable with their states standards. Some of the agencies include: Water Commission, Department for Environmental Protection, State Environmental Protection Agency, Department for Environmental Resources, Department for Environmental Conservation, and Underground Storage Tank Bureau. The regulators interviewed had various technical backgrounds and several of the regulators interviewed were directly involved in establishing their state's soil cleanup standards (IL, PA, NM, WA).

Action Levels versus Cleanup Levels. Generally, the regulators reported that action levels are those levels of contamination that would prompt further investigation if exceeded. Several states (TX, IL, NY, NM) noted that any release of contamination requires notification and possible site investigation. Many regulators report that cleanup levels, on the other hand, are those levels at which a site would require no further action in the form of cleanup, removal, or monitoring. Because no further action is required if the set "cleanup level" is attained, the cleanup level in most states is same as the action level (KY, DE, VA, WY, WI, ND).

Flexibility in State Cleanup Levels. State regulators were asked to report if their cleanup levels are flexible. This question was asked to determine if a state requires cleanup to a "strict" TPH or compound specific standard, or whether the standards are cleanup goals or recommendations. The 1992 Soils magazine survey, used as a baseline for this research, reported recommended cleanup levels for each state, but did not clarify whether these levels are enforced as strict cleanup criteria.

All regulators interviewed report their state has provisions for flexibility in the levels of petroleum contaminated soil which may be left in place without cleanup. In addition, every state reports that defined criteria must be met in order to leave contamination which exceeds their recommended cleanup levels in the ground. The criteria reported can be divided into two categories: (1) meeting state defined, site specific criteria, and (2) conducting a site specific risk assessment to show no risk to human health or the environment.

Several states [illegible] site specific cleanup provisions for which they will allow contamination above recommended cleanup levels to be left in place. The provisions vary from state to state and the criteria used to make the determinations vary as well. Although approximating a risk assessment, several regulators note that their state defined criteria is different from a full risk assessment. ND is one example. In ND, cleanup decisions are made based on:

(1) location of site in relation to surrounding population,
(2) presence of free product,
(3) presence and proximity of municipal utilities,
(4) potential for migration of vapors,
(5) hydrogeology of the site and groundwater use,
(6) the use and location of wells potentially affected by the release, and
(7) future site use.

Similarly, WY uses site specific data and a fate and transport model to make cleanup determinations. Although similar to a risk assessment, WY states that their approach does not require a risk assessment "the way most people think of a risk assessment."

Other states report that their standards are flexible if cleanup is impractical to conduct. IL, for example, states that their risk management group can "accept as no further cleanup required" sites where cleanup (1) would damage buildings or utility lines, (2) is too costly, or (3) is physically not possible because of technology or excavation requirements. WI also reports that they have the discretion to not require cleanup where contamination is impossible to remove.

New Mexico is an example of a state that has well defined criteria for site cleanup. Any underlying groundwater containing 10,000 ppm total dissolved solids (TDS) is considered non potable. Petroleum contaminated sites lying above such acquifers do not require cleanup. In addition, all sites where the interval between contaminated soil and groundwater is fifty feet or greater do not require cleanup.

Rhode Island has provisions for flexibility which may drive cleanups based on non-risk factors. RI considers land usage and aesthetic factors in establishing cleanup level. RI believes that odor problems will be eliminated if TPH is remediated to levels less than 50 ppm . According to RI, a risk assessment will not address the "aesthetics", which is a factor when land usage comes into play. Although RI states they are flexible on their cleanup levels, it appears that the state relies very heavily on TPH levels in soil. Subsequently, actual flexibility allowed by the state appears to be limited.

A second type of criteria mentioned for allowing flexibility in cleanup levels is provisions for risk assessments to justify the amount of contamination that may be left in soils. Half of the states noted that they have criteria for flexibility based on a site specific risk assessment (KY, DE, VA, WY, IL, PA). Associated with assessing risk, several states (IL, PA, NM, NY, WA) state that a responsible party must show that the levels of contamination left at a site will not cause degradation of groundwater. Examples of criteria used to determine potential for groundwater degradation include: depth to groundwater, distance to downgradient drinking water wells, and type of aquifer below a site (NY).

The fact that all regulators report flexibility in their cleanup requirements is significant because it shows that states may approve different types and levels of contamination which may be left in the soil. Although all states report this flexibility, however, it is not clear to what extent the states actually allow or use flexibility provisions.

Texas is an example of a state that has provisions in their soil cleanup regulations for flexibility, but in practice, required cleanup to a non-flexible standard. In the past, TX regulators "pretty much" required any TPH in the ground to be cleaned up.

Use of Risk Assessments for Cleanup. This question was asked to obtain an understanding of (1) whether a state requires a risk assessment for site closure, and (2) whether a state allows a responsible party to conduct a risk assessment to support a site closure decision. The interviewees responses indicate that: (1) two states require risk assessments, (2) all states allow risk assessments, (3) some states do not often use risk assessments and (4) three states are moving toward a more risk based approach for regulation.

Of the states surveyed, two states indicate that they require a risk assessment before the state will allow no further action at a petroleum contaminated site (DE,VA). DE requires a risk based, site specific investigation at all sites where measured levels of petroleum exceed the state's action levels. The results of investigations are reviewed by the state, and the state then determines if cleanup is required. Similarly, VA requires a site characterization report (SCR) for all sites with a confirmed release of petroleum or with TPH concentrations above 100 ppm. The SCR must contain a risk assessment with technical recommendations for an appropriate endpoint for cleanup, based on risk.

Although only DE and VA report that a risk assessment is required prior to site closure, every state interviewed allows a risk assessment to support site cleanup decisions. From the responses, one state could be classified as "encouraging" the use of risk assessments (TX), while others could be classified as not encouraging their use (WI, NY).

Texas is revising their soil cleanup regulations. In the future, risk assessments will likely be conducted for cleanup of all petroleum contaminated sites. WI, on the other hand, discourages risk assessments. WI reports that a policy of conducting risk assessments at every site is unrealistic. Furthermore: (1) risk assessments create an excess financial burden, (2) the state does not have confidence in the results of a risk assessment, and (3) the state does not have the manpower to oversee them.

New York also discourages risk assessments. NY expects responsible parties to clean up a contaminated site as much as possible before a risk assessment is performed. The state will only accept a risk assessment to justify leaving levels of contamination exceeding NY's recommended cleanup levels after cleanup action has been taken. NY believes that risk assessments are often conducted by responsible parties to avoid costly cleanups. Furthermore, private industry encourages the opposite approach, whereby risk assessments are conducted first to establish a target cleanup value. Sites are then cleaned up to this value. NY questions this approach; "if a responsible party can clean a site to cleaner levels, why should they stop at a risk based level?" According to NY, cleanup levels established by conducting risk assessments are, in almost all cases, less stringent than established cleanup levels.

Finally, it is significant to note that three states have or are changing their concept of using risk assessments. As mentioned above, TX is changing their state regulations, and believes that a risk assessment will be performed for cleanup of most petroleum contaminated sites. Although NY currently discourages risk assessments, the state is beginning to look at risk assessments and the regulator interviewed believes that they will be more common in the future. Finally, PA reports that in the past the state did not allow risk assessments because they were used improperly. According to PA, responsible parties would conduct risk assessments in order to justify leaving contamination in place, as opposed to cleaning a site to the lowest levels that can be met. PA, however, now allows risk assessments to justify cleanup determinations. The change in the attitude reflected by these states is a possible indication of a trend away from strict, non flexible, cleanup levels and towards more common use of site specific risk assessments.

It is significant that all of the states interviewed have some type of provisions to accept risk assessments to justify site cleanup decision. This type of flexibility is important because it provides a mechanism for justifying use of specific compound indicators to make cleanup determinations, as opposed to using TPH. In addition, these provisions provide a legal mechanism for deviating from cleanup requirements based on TPH, and instead justifying use of a standard based on compound specific indicators.

Use of TPH for Assessing Risk. Regulators were asked to report if their state considers TPH levels in assessing risk when a risk assessment is used for making cleanup determinations. This question was asked to determine if TPH would drive cleanup at sites where risk based chemicals either did not exist, existed under state recommended cleanup levels, or existed at levels which would not present risk. The goal of this question was to determine whether states use TPH analysis for assessing risk, and if so, why.

Of the states interviewed, seven regulators report that TPH levels are considered when assessing risk. Six regulators report that TPH is not considered. These states are identified in Table 11.

Of the seven states that report using TPH for assessing risk, six states consider TPH levels for assessing risk associated with both gasoline and heavy fuel sites. One state (NM) specified that TPH levels are considered for sites contaminated with diesel only. PA offered the following rationale for using TPH to assess risk: TPH is used to ensure all risk based compounds are removed from a site because cleanup values have not been established for any other compound other than BTEX and TPH.

TABLE 11

STATES WHICH REPORT USE OF TPH FOR ASSESSING RISK

State	Use TPH
Delaware	X
Illinois	
Kentucky	
North Dakota	X
New Mexico	X
New York	
Pennsylvania	X
Rhode Island	X
Texas	
Virginia	
Washington	X
Wisconsin	X
Wyoming	

Six states that use TPH to assess risk have either gasoline or diesel cleanup standards based on TPH only (DE, ND, NM, RI, WA, WI). Since analysis is not required for specific compounds under a TPH standard, it appears that in some cases a state may use TPH for making risk based determinations because TPH is the only analysis required. Similarly, four states that do not use TPH analysis for assessing risk have cleanup standards based on specific compounds only (KY, IL, NY, NM).

The responses to this question are significant because they provide an indication about the flexibility states might have in the use of TPH for making site cleanup determinations. The existence of six states that do not consider TPH levels in evaluating risk at a petroleum contaminated site supports an argument that TPH is not appropriate for evaluating risk. The fact that seven states use TPH for assessing risk, however, supports an opposing argument that TPH can be used to assess risk associated with a petroleum contaminated site. This finding is significant, because it indicates that many states might support the use of TPH and reject a compound specific only standard. DE, is an example. DE reports that the state would not feel comfortable using a compound specific standard, without analysis for TPH, because of the other hydrocarbons which might be left in the soil.

Regulation of Jet Fuel Contaminated Soil. Regulators were asked to report how jet fuel is regulated in their state. This question was asked because standards for jet fuel are not reported in existing literature. Furthermore, this information is required for an understanding of the regulatory requirements the Air Force must meet in cleaning up their sites.

Analysis of the responses shows a wide variance in the category of fuel in which each state places jet fuel. This variance reflects the wide differences in how petroleum cleanup standards vary from state to state. Jet fuel is characterized in the following five categories:

(1) As gasoline (DE, KY, PA, WA)
(2) As diesel or a middle distillate fuel (VA, WI, RI)
(3) As a fuel oil or heavy fuel (NM, NY, WY)
(4) General - state has no separate guidelines for different petroleum products (ND, TX)
(5) Compound specific analysis used (IL)

Figure 1 shows a distribution of the categories in which regulators place jet fuel for soil cleanup.

Five different approaches for regulating jet fuel in thirteen states clearly illustrates the differences in how individual states approach regulation of petroleum contaminated soils. These results may have negative implications for the Air Force because of the difficulty it could create in developing a standardized Air Force approach for remediating jet fuel contaminated sites.

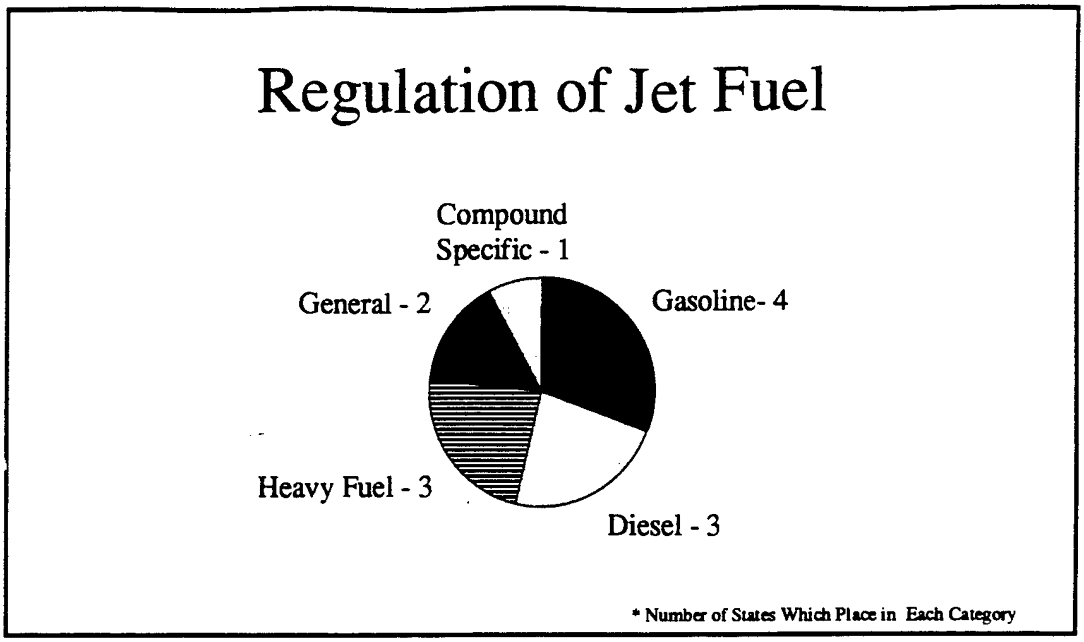

Figure 1

Plans to Change State Standards. State regulators were asked to report if their state has plans to change their soil cleanup standards and, if so, to describe any proposed changes. This question was asked to determine general trends in soil regulation. Of the thirteen states interviewed, four states report plans to change their soil cleanup standards (TX, WY, WI, NY). In addition, one state reports that they are currently evaluating their standards for change (WA). A significant finding is that these states are all moving towards incorporating into their soil regulations either (1) compound specific cleanup requirements or (2) a risk based approach.

Again, TX is moving from strict cleanup levels to a risk based approach for cleanup. In the future, TX will look solely at the risk to public health because of the significant savings which will result in cleanup costs. TX provides a sound rationale for a risk based approach:

> Low cleanup levels are the most conservative and are the safest, but are also the most expensive. What TX is doing is cutting the expense to the bare minimum necessary to protect public health and safety. This will mean that contaminants will be left in the ground. The health and safety risks, however, will be taken care of to where the risk is an acceptable risk.

In the past, WY relied on TPH analysis for making cleanup determinations. The state is now, however, moving towards a compound specific standard with a risk based approach for making site cleanup determinations. WY states that in their proposed guidance, specific compounds will be used for assessing risk, and a compound specific calculation method ba[illegible] groundwater and health considerations will be used to evaluate risk.

WA and WI are other states that are moving towards compound specific standards or a more risk based approach. WA is currently attempting to determine the best methods for performing risk assessments. WI is in the process of establishing cleanup levels for specific compounds. TPH will be used for screening in WI's future standard, but a compound specific standard, which will include BTEX, will be used for cleanup.

<u>Basis for State Cleanup Standards.</u> State regulators were asked to explain the basis for their state's cleanup standards. This question was asked to characterize the rationale behind the development of the soil cleanup standards and to identify considerations important in selecting indicators of petroleum contamination.

The responses were varied. Some regulators list several factors considered or used in the development of their standards, while other regulators report only one criteria or basis. The basis reported by the states can be grouped into the following categories: (1) standards established based on risk criteria, (2) standards established based on another state's approach and/or from a review of the literature, and (3) standards established based upon an extension of a technical basis (i.e., laboratory detection limits or a multiple of groundwater standards). Table 12 provides a breakdown of the basis reported by each state.

TABLE 12

REPORTED BASIS FOR STATE STANDARDS

Basis	DE	IL	KY	ND	NM	NY	PA	RI	TX	VA	WA	WI	WY
1) Risk Criteria													
- Protection of GW		X	X		X	X	X				X		X
- Protection of Human Health			X			X					X		X
- Risk Assessment			X				X			X			
2) - Another State/Review of Literature	X			X	X			X			X		X
- California LUFT Manual									X				
- Stockman & Dime Study	X									X	X		X
3) - Multiple of GW Standard		X											
- Laboratory Detection Limits			X				X					X	
4) - Other (Or not stated)									X		X	X	

The most frequent basis reported is that standards were established based on risk criteria. The following is a list of responses which can be grouped into this category:

(1) standards established for protection of groundwater,
(2) protection of human health,
(3) based on risk assessments, and
(4) developed using modeling.

Of these responses, protection of groundwater is the most frequent response (reported by seven interviewees).

The second most frequently reported basis is soil cleanup standards were developed based on another states approach or developed using information contained in the literature. Six of the thirteen states report this as the basis for their state's cleanup standards. The researchers asked each regulator specifically if their soil cleanup standards are based on the California Leaking Underground Fuel Tank (LUFT) manual or New Jersey's Stokman and Dime research. Four states report that their standards are tied to Stokman and Dime's research (DE, VA, WA, WY), and one state (TX) reports that their standards are based on the California LUFT manual. This question was also asked of the technical experts interviewed. Of the four experts surveyed, two state that the use of TPH as a cleanup criteria was derived from the California LUFT manual (Miller and Bauman) and two attribute the standard to Stokman and Dime's research (Potter and Kostecki). References to the California LUFT manual and Stokman and Dime's research are important and should be considered in the evaluation of the use of the 100 ppm TPH cleanup standard.

Lastly, four states report that their standards are based on laboratory detection limits (KY, PA, WI) or a multiple of their state's groundwater standards (IL). It is also interesting to note that two states report that there is no technical basis in the numbers used for their standards, other than that their cleanup approach is based on best professional judgment (WA, WI).

Advantages of a TPH Cleanup Standard. All state regulators and experts interviewed were asked to provide their technical opinion on advantages and disadvantages of both a TPH cleanup standard and a compound specific cleanup standard. Although information exists in the literature on this subject, the researchers posed this question to (1) obtain and characterize regulatory opinions which could influence how individual state regulators regulate cleanup in their state, (2) compare the application of a TPH cleanup standard against a compound specific standard, and (3) obtain information not available in the literature.

Most of the information presented below was provided by interviewees in response to questions posed to them on this subject. Many interviewees, however, reported benefits and drawbacks of one standard or the other at other times during the interviews. The researchers took the liberty of incorporating these responses into the appropriate section below.

Responses provided for advantages of a TPH cleanup standard can be grouped into categories and ranked by order of frequency. The most common responses are: (1) the TPH method is inexpensive, (2) the method is simple and easy to perform, (3) a TPH standard is a good target level to eliminate risk, and (4) TPH is a good indicator of contamination. Other categories include: (5) TPH may indicate the presence of mobile compounds, (6) TPH reports a wide range of contaminants, and (7) TPH is good from a public perception standpoint. Table 13 summarizes the responses provided by each interviewee.

TABLE 13

ADVANTAGES OF A TPH STANDARD

	State Regulators												Experts				
Advantages	DE	IL	KY	ND	NM	NY	PA	RI	TX	VA	WA	WI	WY	RM	BB	TP	PK
Inexpensive		X				X	X		X			X	X	X	X	X	
Simple method		X		X			X		X			X	X		X	X	
- Quick		X				X	X										
Good Indicator of Contamination	X				X			X	X	X		X	X	X			
- Good target to eliminate risk				X	X			X		X	X		X	X	X		
- Reports Wide Range of Contaminates				X	X		X				X				X		
May indicate mobile contaminants	X				X					X	X				X	X	
Public Perception							X									X	X
May indicate Contamination Elsewhere	X													X			
Aesthetics/Odors will be Removed								X		X							

Nine interviewees report low cost as an advantage of the TPH standard. The method is cheaper than methods used to identify levels of specific compounds, and provides a low cost indication of what might be in the soil (WY). In one state, investigation and cleanup of a site using TPH is perceived by responsible parties to be less expensive then attempting to justify higher levels through a compound specific investigation and risk assessment. PA reports that although the state has an allowance for risk assessments, through which responsible parties can avoid the 100 ppm TPH cleanup standard, "people just do not want to put the money into it." Responsible parties are complying with the state's 100 ppm TPH standard rather than performing risk assessments to justify leaving higher levels of TPH in the soil.

Eight interviewees report that the TPH method is simple and easy to perform. Eight interviewees also report that TPH is useful as a target to eliminate risk. Several interviewees expressed that if a petroleum contaminated site is cleaned up to 100 ppm TPH level then most, if not all, health hazards associated with the site will be removed. For instance, according to WY: "if a site can meet the TPH criteria (50 to 100 ppm depending on the location of groundwater), we hypothesize that it [contamination left at the site] will be well within the criteria of any BTEX concentration." Potter supports this viewpoint and believes that the TPH standard may even be more conservative than compound specific standard.

Eight individuals state that an advantage of using TPH is that it is a good indicator of contamination. Several interviewees indicate they are comfortable with using TPH as a standard for the heavier petroleum products because they believe the analysis provides a good representation of what is in the ground. Some states also note that use of TPH for petroleum products other than gasoline is appropriate because indicator compounds have not been adequately established for those products. According to NM, "TPH is good for different mixtures such as waste oil, kerosene, and diesel that do not have target compounds such as BTEX." DE reports "with heating oils and diesel, TPH analysis represents close to 100% of what is in those fuels."

Another reported advantage of a TPH standard is that a TPH analysis measures a wide range of compounds. Five interviewees perceive the TPH standard to be beneficial because it represents most of the hydrocarbons in petroleum. ND notes, for instance, that TPH provides information on the entire range of petroleum compounds, as opposed to just BTEX. This advantage is closely associated with one of the most commonly stated disadvantages of a compound specific standard: that a compound specific standard requires measurement of only a few chemical compounds, and that not enough is known about petroleum to ignore all but a few indicator compounds (WA). This and other disadvantages associated with a compound specific standard is discussed in the next section.

When asked to comment on whether TPH could be used to indicate the mobility potential of contamination in the soil, the responses were divided. Some interviewees state that TPH analysis can be used to indicate the presence of mobile compounds, while others state that it can not. Bauman provides insight into why different viewpoints exist. According to Bauman, method E418.1 does not give any real indication of mobility or leaching potential of petroleum. This is because the method does not distinguish between the different hydrocarbons that make up petroleum. Bauman states, however, that if a gas chromatograph method (8015, 8020, etc.) is performed and a boiling point distribution is recorded, a TPH analysis may provide *some* indication of mobility and/or leaching potential of the contamination. A general inference can be made based on the distribution of the hydrocarbons reported.

The use of TPH to obtain an indication of the presence of mobile compounds, therefore, appears to depend on the analytical protocol used. According to WA, WA's analytical protocols assess specific fractions of TPH, and the lighter fractions are considered more mobile than the heavier fractions. Although some interviewees report that a general indication of mobility may be determined from a TPH analysis, however, others report that the information TPH provides on mobility potential is limited or nonexistent. According to WI, "TPH does not give you enough information to model contaminant movement or migration to a potential receptor."

Three interviewees state that another advantage of TPH is that the method is well viewed by the public. PA, for instance, says that TPH "gives people a warm and fuzzy feeling that they know what is going on." According to Potter, "people know what it is and people believe that it takes a broad cut at the chemicals that are present [at a petroleum contaminated site]".

Two other interviewees state that use of TPH may be beneficial because it can indicate the presence of contamination elsewhere at a site. In fact, DE requires TPH analysis because the state believes TPH can indicate risk based compounds (BTEX) which may not be detected in initial samples taken at a site. DE provides an example of a site investigation where TPH was detected in soil with very low levels of BTEX. Because TPH levels exceeded DE's established standard, the state required additional investigation at the site. Upon further investigation, high levels of BTEX were found which would not have been discovered if only a compound specific standard had been used.

Miller explains that the use of TPH to indicate the presence of contamination elsewhere at a site was the reason the TPH standard was developed. TPH is a useful indicator of petroleum contamination and can be used to indicate the presence of BTEX at a site. Miller cautions, however, that TPH should not be used as a strict cleanup standard. If soil at a site is sampled all the way to the water table and no BTEX is found, for instance, TPH levels could drive unnecessary cleanup. Miller states that because the TPH standard was developed to determine the presence of the risk based BTEX components of petroleum, the site should be considered clean if BTEX is not present or meets established cleanup standards.

A final advantage of a TPH cleanup standard, offered by two interviewees, is that TPH will ensure the aesthetic quality of a site. VA believes it is not acceptable to leave high levels of TPH in the ground, even if BTEX levels are negligible, because contamination may cause taste and odor problems in groundwater. VA states "if you cannot drink the water because of aesthetic reasons, it is no more useful than water contaminated with BTEX." RI expressed the same viewpoint:

> By setting a low TPH standard (100 ppm), aesthetics are considered in addition to the risk from the contamination left behind; a number less than this reduces any odor concerns that might exist.

All of the responses listed under advantages of a TPH standard are supported by the literature. The advantages support the use of TPH for both screening and as a strict cleanup standard for petroleum contaminated soil. Furthermore, these advantages explain the popularity of TPH as a cleanup standard.

Disadvantages of a TPH Cleanup Standard. Responses provided by interviewees for disadvantages associated with the use of a TPH cleanup standard are categorized below in Table 14. The most common category of response is that TPH cannot be used to measure risk. Three responses are grouped into this category: (1) TPH cannot be used to measure risk, (2) no toxicological values exist for TPH, and (3) TPH does not identify specific compounds. The second most common response is that problems exist with the TPH analytical methods. Other commonly reported disadvantages include: TPH doesn't indicate contaminant mobility potential, and TPH is not appropriate for gasoline.

A majority of those interviewed (eleven interviewees) state that TPH analysis cannot be used to measure risk. Interviewees state that a direct measurement of risk associated with petroleum at a site cannot be obtained using TPH because TPH analysis

TABLE 14

DISADVANTAGES OF A TPH CLEANUP STANDARD

	State Regulators													Experts			
Disadvantages	DE	IL	KY	ND	NM	NY	PA	RI	TX	VA	WA	WI	WY	RM	BB	TP	PK
Cannot be used to Assess Risk			X	X			X	X	X	X		X	X	X	X		X
- No Toxicological Values for TPH							X			X	X		X	X			X
- Does not ID Specific Compounds			X	X			X		X				X	X	X	X	X
Problems with Analytical Method		X	X		X	X		X	X					X	X	X	
Doesn't Indicate Contaminate Mobility				X					X	X		X			X		X
TPH is not Appropriate for Gas					X					X				X	X		
Little Scientific Basis for the Numbers						X									X		
May Leave Contaminants in Soil		X															
Can Drive Unnecessary Cleanups														X			
Cannot evaluate BTEX Concentrations			X														

provides results for a large number of different chemicals, but does not identify specific compounds. Several interviewees also state that there are no established toxicological values for TPH. This is because of the type of results the analysis provides and because each different petroleum product is made up of different compounds. Several regulators and experts state that in order to measure risk at a site, a compound specific analysis must be performed.

Nine interviewees note problems associated with the TPH analytical method. The following problems are identified:

(1) Problems with false negatives and false positives,
(2) TPH will measure waxes and paraffin's which do not present risk to human health or the environment,
(3) TPH will measure natural organics in the soil,
(4) TPH detection can be fooled by fine particulates,
(5) the TPH method is not good for aromatics because volatiles are often lost during preparation, and
(6) too much variability exists in the TPH methods.

According to Bauman, the 418.1 and California methods for TPH analysis are poorly written. Bauman states that these methods allow a lot of variability in the way the tests are run and in how the results of the analysis are interpreted. Because of this variability, "you may send a sample to a dozen different labs to do 418.1 and they may come up with numbers that differ by an order of magnitude or a couple of orders of magnitude." Miller also identifies problems with the 418.1 method. He states that the petroleum mixture required by Method 418.1 to calibrate laboratory equipment has no similarity to the petroleum found at Air Force petroleum contaminated sites.

The use of TPH to indicate the presence of mobile fractions of petroleum was discussed above. An equal number of interviewees who stated that TPH could be used to indicate mobile contaminates stated that TPH cannot be used to determine the presence of mobile contaminants. Again, the discrepancy in the responses appears to be correlated to the analytical method and the type of results reported.

Several individuals state that a TPH standard is not appropriate for gasoline (NM, VA, Miller, Bauman). VA believes that a TPH cleanup standard cannot be used without requiring analysis for specific compounds, because TPH does not measure the BTEX components. According to VA, both TPH and BTEX should be measured at gasoline spill sites. Bauman reports that TPH "doesn't make sense for gasoline contamination." He believes that BTEX criteria should be used and should drive cleanup at gasoline contaminated sites. Miller believes that a TPH standard is not appropriate for either gasoline or diesel. It is significant that these interviewees believe TPH should not be used for gasoline because of the number of states which use TPH as the sole cleanup criteria for gasoline contaminated soils.

The responses listed above were mentioned by four or more interviewees. Other disadvantages are noted by one or more interviewees. NY and Bauman report that there is little scientific basis in the TPH standards. IL states that a disadvantage of TPH is that the use of a TPH standard alone will not ensure the protection of groundwater. IL believes that even if soil is cleaned up using TPH criteria, compounds such as BTEX may still be present in quantities that could contaminate groundwater. KY also notes that a disadvantage of a TPH cleanup standard is that BTEX concentrations are not evaluated.

Miller provides a final disadvantage associated with a TPH standard: cleanup to strict TPH levels can drive unnecessary cleanups. According to Miller, studies such as the study reported in the California LUFT manual, have established levels of BTEX which can be left in soil without causing degradation of groundwater. Miller states that (1) there is not much BTEX left in the majority of the Air Force sites and (2) BTEX can be preferentially removed through technologies such as bioventing. As a result, Miller states that a TPH cleanup standard can drive cleanup of sites that would not require cleanup under a BTEX standard. Furthermore, because BTEX may be preferentially removed with technologies such as bioventing, sites requiring remediation could be cleaned up much faster and at a lower cost.

Use of Different TPH Cleanup Levels. Interviewees were asked to report whether they believe, if a TPH cleanup standard were to be used for cleanup of a petroleum contaminated site, different cleanup levels are appropriate for different petroleum products. Gasoline and diesel were suggested as example petroleum products. The researchers asked this question to identify the rationale behind why some states have different standards for different types of petroleum, while other do not.

The responses are varied. Roughly half of the interviewees report that different TPH cleanup levels are appropriate, and the other half report that different levels are not. Bauman provides a rationale for establishing separate standards for different petroleum products. Different types of petroleum have different types of constituents, with different potential for mobility [in the ground]. Because of this, Bauman believes that separate standards for gasoline, middle distillates, and heavy fuels "makes sense." Kostecki presents an opposing viewpoint. According to Kostecki, the scientific community does not know enough about the fate and transport of the constituents of petroleum. Furthermore, there is too much variation in the makeup of individual products. Separate standards, therefore, may not be appropriate.

Advantages of a Compound Specific Cleanup Standard. State regulators and experts were asked to present their technical opinion on advantages and disadvantages associated with the use of a compound specific standard. As part of their response, each interviewee was asked to address risk and mobility considerations. This question was asked to obtain information necessary to evaluate the application of a compound specific standard for cleanup of petroleum contaminated sites. Responses presented as advantages are characterized below.

The most common category of advantages reported is that a compound specific analysis can be used to indicate risk to human health and/or indicate the threat to groundwater. The following three responses are grouped in this category: (1) a compound specific analysis can be used to assess risk, (2) specific compounds are measured, and (3) toxicological data exists for specific compounds. The second most frequent category of response is (4) a compound specific standard provides the opportunity to focus on indicator compounds and mobile contaminants. Other reported advantages are: (5) contaminants which present risk are removed, and (6) cost savings are incurred if used instead of a standard based on TPH. Table 15 presents a summary of these categories.

Nine interviewees report that a compound specific analysis can be used to measure risk. Some interviewees note that under a compound specific standard, individual levels of specific compounds can be measured to which toxicological data can be compared (PA, MN, WA, VA). A risk assessment, therefore, can be conducted based

TABLE 15

ADVANTAGES OF A COMPOUND SPECIFIC STANDARD

	State Regulators													Experts			
Advantage	**DE**	**IL**	**KY**	**ND**	**NM**	**NY**	**PA**	**RI**	**TX**	**VA**	**WA**	**WI**	**WY**	**RM**	**BB**	**TP**	**PK**
Can be Used to Measure Risk					X	X	X		X	X		X		X	X		X
- Measures Specific Compounds			X	X									X	X	X		
- Toxicological Data Exists to Compare				X	X		X			X	X		X	X	X		
Allows Focus on Indicator Compounds								X								X	X
Allows Focus on Mobil Contaminants		X							X			X				X	X
Can Remove Contaminants of Risk					X												
- Remove Benzene and Risk is Removed													X				
- Remove BTEX and Risk is Removed														X			
Cost Savings for Cleanup														X			

on actual numbers. Bauman notes that because almost all risk calculations are based on specific compounds, it makes sense to have compound specific standards.

Many interviewees also report that an advantage of a compound specific standard is that it allows a focus on indicator compounds which, in turn, can be used to assess risk and mobility of the contamination. Kostecki states that because of the relative mobility of certain constituents it may be appropriate to focus on the mobile constituents if groundwater contamination is a concern. In addition to mobile compounds, some non-mobile compounds found in the heavier fraction products may be of concern if soil ingestion is anticipated. Generally, most interviewees show support for the use of indicator compounds.

Seven interviewees support the use of BTEX or benzene as an indicator of petroleum contamination. Several reasons are given for using BTEX. These reasons include: (1) BTEX is a good representation of gasoline contamination (RI), (2) BTEX is the most mobile fraction of petroleum (WY), (3) BTEX allows modeling of contaminant mobility and potential for contaminants to contaminate groundwater (WI), and (4) there is a known health hazard associated with BTEX (VA).

Several interviewees also identify polynuclear aromatic hydrocarbons (PNAs) as a possible indicator compound for petroleum. Interviewees comment, however, that although PNAs may be just as toxic as the BTEX compounds, they are not nearly as mobile. Bauman, for instance, states that because the multi-ring and longer chain hydrocarbons are less mobile and less soluble, they have less of a potential to contaminate groundwater. PNAs therefore, present less risk.

Some interviewees commented that an advantage in using a compound specific standard is that, by analyzing for specific indicator compounds, the contaminants of risk may be removed. In fact, two interviewees report that a compound specific standard is more protective of human health (NY, Kostecki). NM assumes that, if the standard for benzene is not exceeded, then the rest of the aromatic hydrocarbons (and petroleum) will not exceed risk levels. IL is confident that their compound specific soil objectives will ensure that soil will be cleaned up to be protective of groundwater. Furthermore, WY states that if you "take care of benzene... you'll take care of everything else in the process." Some interviewees, however, support the use of BTEX as an indicator compound for gasoline only. They note that diesel and the heavier hydrocarbons contain other compounds which might be left behind if only BTEX is analyzed.

As discussed previously, Miller provides a strong argument for using a compound specific standard as opposed to a TPH based standard. Use of a compound specific standard might result in significant cost savings. Although Miller and TX are the only interviewees who identified cost savings associated with the use of a compound specific standard, the cost implications might be significant and should not be overlooked.

Disadvantages of a Compound Specific Cleanup Standard. Interviewees provide many disadvantages associated with using a compound specific standard. The most common disadvantage is that (1) under a compound specific standard, not all hydrocarbons are measured. Many interviewees expressed concern about the contaminants that might remain if a standard which requires analysis for only specific compounds is used. Other disadvantages reported include: (2) additional costs are associated with this type of standard, (3) a compound specific standard creates additional requirements in work and time, and (4) such a standard can drive more cleanups (if set too low). A breakdown of the responses provided by each interviewee is shown in Table 16.

TABLE 16

DISADVANTAGES OF A COMPOUND SPECIFIC STANDARD

	State Regulators													**Experts**			
Disadvantage	**DE**	**IL**	**KY**	**ND**	**NM**	**NY**	**PA**	**RI**	**TX**	**VA**	**WA**	**WI**	**WY**	**RM**	**BB**	**TP**	**PK**
Does not Measure all Hydrocarbons	X			X						X	X					X	
- Cannot Ignore other Contaminants	X									X	X					X	
- Harmful Contaminants May Remain				X													
- Uncertainty about other Constituents										X		X					
- Debate about Compounds to be Used																	X
Cost for Analysis						X	X		X				X	X	X		
Additional Work and Time						X			X				X				
Can Drive More Cleanups		X			X			X									

Many state regulators and technical experts note that under a compound specific standard, not all hydrocarbons are measured. This response expresses a primary concern by many interviewees that even if the risk based BTEX compounds are remediated, other compounds would be left in the soil, which might present risk. Sub-categories of this response include: (a) it is not appropriate to ignore contaminants other than a few indicator compounds measured; (b) other harmful contaminants may remain in the soil; (c) there is uncertainty about the hazards associated with other hydrocarbons; and (d) there is currently a debate about which compounds should be used as indicator compounds.

Several interviewees note that it is impossible to use one or more indicator compounds to represent petroleum contaminated soil. WA states that data on specific compounds only represents a very small fraction of the entire range of petroleum and that not enough is known about all of the other constituents to ignore all but just a few. Furthermore, "using a few compounds to represent the entire range of petroleum can grossly over- or under-estimate the toxicity." WI also states that the specific compound analyzed may not be a good indicator of the type of petroleum contamination.

According to Kostecki and VA, the variability in the composition of individual petroleum products make it difficult to identify, with certainty, the compounds that represent the hazards associated with a petroleum product. Kostecki further states that for some fuels, experts still debate which indicator compounds are appropriate. ND states that "focusing on specific contaminants for one petroleum product may not apply to other petroleum products... concern is that some potentially harmful constituents will be overlooked." Furthermore, ND states "if you use just BTEX for your cleanup standard...you'll possibly be leaving behind some of the heavier fractions." The concern that a compound specific analysis does not measure all hydrocarbons is clearly the greatest concern reported by interviewees for using a compound specific standard.

In a different category of disadvantages reported, six interviewees note that a compound specific standard is more costly than a TPH based standard. Most of these interviewees report that the cost to analyze for specific compounds is significantly more expensive than the cost for TPH. PA provides another concern. According to PA, under a compound specific standard "cleanup values should be established for all parameters in the petroleum product for which toxicological data exists." Analytical costs for a compound specific standard would, therefore, be significantly more expensive because three or four different analytical methods would be required.

Another reported disadvantage is that if a compound specific standard is set too low, it could drive more cleanups (NM). IL mentioned that because of the extremely low cleanup standards which are set by the state, petroleum marketers are going to the legislature to attempt to have them changed.

Finally, three regulators comment that a compound specific standard places more demand on the time of regulators and consultants (TX). NY states that a compound specific analysis takes more time for laboratory analysis, and WI reports that a compound specific analysis requires a more detailed effort because there are more "things to look at".

<u>Chemical Compounds for a Compound Specific Standard.</u> Interviewees were asked to report, if a compound specific standard is used, the chemical compounds they believe should be included, by petroleum product. Common responses are reported here. Four interviewees do not make a distinction between the type of petroleum, but state that BTEX and polynuclear aromatic hydrocarbons should be used in a compound specific standard. For those that did distinguish between types of petroleum, seven interviewees support the use of BTEX gasoline, and three support MTBE for gasoline. For diesel naphthalene (4 interviewees) and polynuclear aromatic hydrocarbons (three interviewees) were suggested as chemical indicators. The chemical indicators mentioned by the

interviewees reflect the same chemicals actually used in state standards (as listed in Chapter IV).

Interviews with Technical Experts

Most of the questions posed to the experts are incorporated and summarized in the previous section. This section reports responses to questions that are not included above. The additional questions address the (1) importance of risk assessment for establishing cleanup standards, (2) risk assessment criteria experts believe to be most important in developing a petroleum cleanup standard, and (3) appropriateness of a strict TPH standard for cleanup of petroleum.

Importance of Risk Assessment in Development of Standards. This question was asked to obtain technical opinions on the relative importance of the risk assessment process in developing standards for petroleum contaminated soil. Three experts (Miller was not asked to comment) report that they are strong proponents of using risk based criteria for the development of soil cleanup standards.

Bauman and Kostecki note that the use of generic cleanup standards based on strict cleanup guidelines is an alternative to a site specific cleanup approach. Bauman notes that the numbers used by many states for TPH and BTEX "for the most part are not well based on science." Furthermore, he notes that states that have attempted to use a scientific approach to setting cleanup standards typically make worst case assumptions, implying that many standards are very conservative. Similarly, Kostecki states that due to the conservative assumptions used by most states in establishing cleanup standards, the majority of petroleum contaminated sites are being cleaned up to overly conservative levels. Furthermore, use of risk assessment is more cost effective because overly conservative assumptions are not used, and cleanup activities are "tailored" to a specific site.

Risk Assessment Criteria Important for Cleanup Standards. Three experts were asked to report the risk assessment criteria they believe are most important in establishing a petroleum cleanup standard. Bauman states that the existing quality and use of groundwater which might be impacted from a petroleum contaminated site is the most important consideration. According to Potter, the most important consideration is exposure. Potter notes that in order to evaluate exposure one must evaluate the toxicity of the contaminant and the factors that effect transport of the contaminant to receptors. Kostecki agrees with Potter and states the most important criteria for evaluating risk are the toxicity of the source and the potential routes of exposure.

Use of a Strict TPH Cleanup Standard. All four experts were asked to comment on whether they believe it appropriate to require cleanup of a petroleum contaminated site to a strict TPH cleanup level. Three experts interviewed report that a strict level is not appropriate, while one reports that a strict TPH cleanup level may have some merit. According to Potter, Kostecki, and Miller, a TPH standard is not appropriate because (1) it is not based on risk to human health and (2) because of the problems associated with the TPH analytical method. Both Potter and Miller also note that use of a strict TPH cleanup standard can drive unnecessary cleanups. Bauman, on the other hand, states that a TPH cleanup standard may have some merit for fuels that do not contain BTEX, because a TPH standard will, in most cases, ensure removal of health hazards associated with the fuel.

Conclusions

The information provided in this chapter helps to characterize and explain the standards used for cleanup of petroleum contaminated soils, and provides information to compare the application of a TPH standard against a BTEX standard. This chapter presents several significant findings.

First, all states interviewed report flexibility in their standards for leaving contamination which exceeds recommended cleanup levels in place. All states also report provisions in their standards for allowing a risk assessment to justify site cleanup determinations. This finding is significant for proponents of using a compound specific standard. No state regulations or laws require the application of a TPH standard or prevent the use of a compound specific standard. Room for negotiation, therefore, exists for the actual standard used for cleanup of petroleum contaminated soils.

Second, some states discourage the use of risk assessments. As exemplified by TX, although some states have flexibility in their regulations, actual flexibility allowed by the state may be limited. These may be obstacles proponents of a compound specific standard might face in attempting to justify compound specific cleanup determinations.

Third, many regulators report that TPH analysis is used in their state for assessing risk. The seven states that use TPH clearly support the use of TPH for making cleanup determinations. The viewpoint that TPH can be used to assess risk also presents an obstacle for proponents attempting to justify the use of a compound specific standard.

Fourth, the categories in which jet fuel is placed clearly indicates the non-uniformity in the regulations set for cleanup of petroleum.

Fifth, four of the thirteen state regulators interviewed report that their state has plans to change their soil cleanup standards. All four states are moving towards use of either compound specific cleanup provisions or a risk based approach for their soil cleanup standards.

Sixth, six interviewees attribute soil cleanup standards to Stokman and Dime's research and three attribute the standards to the California LUFT manual. This is significant because the basis for these studies assumes (1) risk associated with a petroleum contaminated site is based on BTEX, and (2) assumes a constant relationship between BTEX and TPH. The second assumption will be challenged in Chapter VI.

Seventh, all of the advantages reported for using a TPH cleanup standard support its use for both screening and as a strict cleanup standard. These advantages also explain the popularity of the standard. The majority of the disadvantages reported for using a TPH standard, however, do not preclude its application as a cleanup standard. Although the method cannot be used to measure risk, interviewees believe remediation of a petroleum contaminated site to a strict TPH level will eliminate the risk associated with the site. This belief is supported by the literature. Although many interviewees note problems with the analytical method for TPH, these problems are resolved by the levels for which TPH standards are set.

The one major disadvantage reported with the use of a TPH standard is that its use can drive unnecessary site cleanups. This one disadvantage may outweigh all of the advantages associated with a TPH standard. According to Miller, the cost savings associated with a compound specific standard, as opposed to a TPH standard, would be enormous. The conservative nature of the TPH standard and an estimate of number of sites which would not require remediation under a BTEX standard, again, are explored in the following chapters.

Finally, advantages reported by interviewees of a compound specific standard support its use for measuring risk associated with a petroleum contaminated site. Interviewees express concern, however, that a compound specific standard will not measure all hydrocarbons, and that if a compound specific standard were used, other compounds might be left in the soil which would present risk. Cost for compound specific analysis is another reported disadvantages which might also have implications for regulatory acceptance of a compound specific standard. These viewpoints, held by many state regulators, may be the largest obstacle for parties who wish to justify the use of a compound specific standard.

VI. IRPIMS Data Analysis and Cost Savings Analysis

Introduction

This chapter provides an analysis of the IRPIMS database information received from the Air Force Center for Environmental Excellence. The main purpose of the IRPIMS data analysis is to investigate the relationship of BTEX to TPH in soils. Specifically, this investigation will determine whether or not the residual soil BTEX concentration assumption used in the California LUFT Manual and by Stokman and Dime is valid for soils contaminated with JP-4. This assumption, as described in Chapter II, is that the percentage of BTEX in soil contaminated with petroleum is the same as in a pre-spilled petroleum product.

The data was first characterized to determine the frequency and levels of BTEX and TPH concentrations measured at Air Force sites, and to determine the number of petroleum contaminated sites sampled for BTEX or TPH. Second, an explanation of why the data proved insufficient to characterize the relationship of BTEX to TPH over time under different hydrogeological site conditions is provided. Lastly, a statistical analysis comparing BTEX to TPH ratios at JP-4 contaminated soil sites to expected average ratios from distilled JP-4 is presented. This subsequent analysis determines whether or not the BTEX components of JP-4 weather faster than all petroleum hydrocarbons (measured by Method 418.1) found in JP-4.

This chapter also estimates the number of Air Force sites that would require cleanup under a TPH cleanup standard and the number of sites that would require cleanup under a BTEX cleanup standard. From these estimates a cleanup cost-comparison is made. This comparison is used to predict the percentage of cleanup costs that would be saved if a BTEX cleanup standard were applied to all Air Force sites versus a TPH cleanup standard.

IRPIMS Data Characterization

As explained in Chapter III, the researchers requested information for all records containing either TPH or BTEX soil sample data from Air Force installations, plants, or bases. First, the data is characterized to show usable versus non-usable information contained in the IRPIMS database for this type of analysis. Second, a discussion of the identifiable sites in the database is made. Included are the total number of identified petroleum sites contained in the database analyzed for either BTEX or TPH. Lastly, a detailed analysis of the known petroleum sites is made to include categories of contamination and overall contamination frequency. The hydrogeological site data received are not used in this analysis because no soil samples for BTEX and TPH were identified in the database at the same site from two or more time periods (see section on relationship of BTEX to TPH for further explanation).

General Description. The requested data was extracted from the IRPIMS database in May 1993. It is important to note that additional information is added to the database on a continual basis. This research, therefore, reflects information contained in the IRPIMS at the time of the request.

The data was provided in three separate ASCII files. The first file contained sample information for all sites where BTEX or TPH analyses was performed and detected on soils above the laboratory detection limit (LDL) identified for the analysis. Information on soil pH and specific conductance is included in this file. Only a small number of the sample results, however, were reported for pH, and none of the samples had results for specific conductance. This limitation inhibited the use of pH and specific conductance information and, therefore, these soil parameters are not used in this analysis.

The second file contained all non-detect sample information for BTEX and TPH analyses. The third file contained existing information on soil lithology, soil stratigraphic order, and soil ASTM classification codes for boreholes in which BTEX or TPH were analyzed. Due to time limitations and data limitations identified in the next section of this chapter, this information is not used in the analysis. Table 17 below, provides a description of obtained data records. Each record in the data refers to one sample analysis.

TABLE 17

SOIL MATRIX RECORDS

Record Description	**Number of Records**		
	Detect	**Non-Detect**	**Total**
TPH Analysis Records	1932	5221	7153
BTEX Analysis Records	1096	6002	7098
Total Soil Matrix Records	3028	11223	14251

Site Identification Analysis. To determine the usefulness of the data for establishing the relationship of BTEX to TPH over time, the data were examined with the goal of comparing samples at the same site from two or more time periods. To accomplish this, two approaches were taken. First, the researchers hoped to identify sites, with the same site name from the same Air Force installation, with sampling data from two or more time periods. If no site name information was provided in a sample record, a second approach was taken. With this approach, site coordinate information was used to determine site location. Samples identified within 100 feet of each other from different time periods were to be considered from the same site. Table 18 below provides a description of the site name and coordinate information contained in the data. As Table 18 shows, twenty-one percent of the data lacked any indication of type, name, or location of site.

TABLE 18

SITE NAME AND SITE COORDINATE INFORMATION

Record Description	**# (% of total)**
Records with <u>NO</u> Site Name or Coordinate Information	3129 (21%)
Records with Site Name or Coordinate Information	11761 (79%)
Total Soil Matrix Records	14890 (100%)

<u>Site Breakdown</u>. To further characterize the data, those records containing site name information were examined. This was accomplished to distinguish petroleum sites from those sites where the type of contamination was unknown. By sorting out records which did not provide site name information, a total of 279 sites were identified. Of the 279 sites, 120 were identified as petroleum sites. If the site name field provided information normally associated with petroleum, the site was considered a petroleum site.

<u>Classification of Petroleum Sites</u>. The data from the identified petroleum sites was further sub-divided by type of contamination or by type of site. This was done because different petroleum products could be expected to have different constituent percentages and, therefore, ratios of BTEX to TPH. Table 19 below presents the results. All records where JP-4 was indicated in the site name were placed in a "JP-4 site" category. Gasoline and fire training areas were similarly categorized. The fuel oil sites all contained the word "oil" in the site name field and where it was apparent that the contamination was not waste oil. The suspected JP-4 contaminated sites contained words such as "POL", "bulk fuel storage", and "tank farm" in the site name field. The rest of the petroleum sites contained words such as "Underground Storage Tank" and "waste oil" in the site name field.

TABLE 19

PETROLEUM CONTAMINATION BY TYPE OF SITE

Description	# of Sites	Number of Records		
		Detect	Non-Detect	Total
JP-4 Contamination	15	138	166	304
Gasoline Contamination	6	24	85	109
Fire Training Areas	40	528	502	1030
Fuel Oil Contamination	6	19	117	136
Suspected JP-4 Contam.	29	275	215	490
Other Petroleum Contam.	24	71	232	303
Total Petroleum Contaminated Sites	120	1055	1317	2372

BTEX to TPH Relationship Over Time and Varying Hydrogeological Site Conditions

As explained in Chapter III, the approach to analyze the relationship of BTEX to TPH in soil over time was a comparison of ratios from the same site over different time periods. For each site with BTEX and TPH data, the researchers planned to evaluate the utility of the hydrogeological information to determine if any correlation could be made to the preferential weathering of BTEX to TPH. The researchers found, through an in-depth analysis of the data, that no site in the database had been sampled at different time periods. The data was, therefore, insufficient for this type of analysis. The procedure used for this analysis with a detailed explanation of why the data is insufficient is described below.

Data Analysis. First, the two ASCII files containing the BTEX and TPH sample measurements were imported into a database program on a personal computer. Both files were then scanned for accuracy and type of data. The purpose of this scan was to ensure that all of the data was lined up by field name. Sixty-eight percent of the sample data was groundwater data. Since the focus of this analysis is on soil contamination, the groundwater records were removed. As stated previously, twenty-one percent of the soil matrix data did not have either site name or coordinate (NCOORD or ECOORD) information. Because determining what particular site the samples came from was not possible, these records were not usable in the analysis. The analysis noted that the site identification information field is only filled in when the site name field contains information and provided no additional information. The site identification information was subsequently ignored.

After removing or deleting the unusable records, the two files were merged. The combined file was then sorted with the primary sort on the Air Force installation code and the secondary sorts on the site name, the north and east coordinates, the sample depth, and the sample analytical method code, respectively. This was accomplished to facilitate locating samples from different time periods. All records from sites that contained only non-detect sample information were then removed from the combined file. These records were removed because BTEX to TPH ratios could not be calculated from sites without initial detection's of BTEX and TPH.

The combined file was then examined for sites with concentrations of TPH and one or more of the BTEX constituents. Following this, the data was examined for samples of both TPH and BTEX at the same site from a different time period. If no site name was contained in a record, the North and East coordinates were used to identify like sites from two different time periods.

Results of Data Analysis. After a complete and thorough review, the researchers found that no data was present in which both BTEX or TPH sample data was identified from the same site at different time periods. Similarly, for the records where no site name was identified, there were no instances where BTEX or TPH sample data from one time period was within 100 feet of a sample from another time period. Should sample data have been found within 100 feet from different time periods, the researchers would have considered the samples from the same site. If sufficient data had been available, the ratios of BTEX to TPH from the first time period would have been compared with the BTEX to

TPH ratios identified at a later date. Since this methodology is inappropriate for the data received, an analysis comparing the ratios calculated from the data to virgin product ratios was developed and implemented. This analysis is described in the next section.

BTEX to TPH Ratio Analysis

Upon determining that the BTEX and TPH sample data contained in the IRPIMS database did not allow a ratio analysis of BTEX to TPH over time, a subsequent approach was developed and implemented. The researchers used only records where the site name information was provided because the type of contamination was impossible to determine otherwise. This method allowed an analysis by type of petroleum product.

For this analysis, the data was broken down by type of petroleum contamination or by type of site (see Table 19). Of the petroleum contamination groupings identified, the JP-4 contaminated sites were selected for BTEX to TPH ratio analysis. The fire training site data, the fuel oil site data, the suspected JP-4 site data, and the rest of the petroleum sites are not analyzed with this method because the type of contamination could not be identified. The gasoline site data was not used because an analysis of this data showed that (1) only eight same-borehole, same-depth samples had data for both BTEX and TPH, (2) the type of gasoline product (leaded, unleaded, premium) at the sites is unavailable in the database, and (3) the wide range of BTEX percentages found in different distilled grades of gasoline did not allow for an accurate virgin product estimate (30a).

JP-4 Site Analysis. Out of the 297 sites identified (site name data provided), fifteen sites have JP-4 indicated in the site name field. The researchers assumed that these sites are contaminated only with JP-4. Of the fifteen JP-4 sites, nine have soil sample data for both BTEX and TPH. These nine sites are used in this ratio analysis.

Description of Analysis. Forty-five benzene (BZ) to TPH and BTEX to TPH ratios were calculated from the JP-4 sites. These ratios were obtained from samples where both BTEX and TPH were analyzed at the same depth and same location (same borehole). The researchers decided to expand their original methodology to include an analysis on BZ to TPH ratios in addition to the BTEX to TPH ratios because (1) several states have soil standards for BZ, (2) the literature identifies BZ as the most toxic, mobile, and soluble of the BTEX compounds, and (3) the literature identifies BZ as the greatest threat to groundwater from petroleum contaminated soils (9;17;35). For simplicity, a "sample" is defined here as one or more records which contain results from BTEX or TPH analyses at the same location and sample depth. Although more than one sample may have been taken to run different analyses for BTEX and TPH, we will consider the individual samples to be representative of the soil present at the same location and same depth. The BZ to TPH analysis is discussed first followed by the BTEX to TPH analysis.

Benzene to TPH Data. The forty-five BZ to TPH calculated ratios were obtained from samples where the analytical method used to measure TPH concentrations detected TPH levels above the indicated laboratory detection limit (LDL). Forty-one other cases were noted where neither TPH nor BZ was detected at the same location and sample depth. These are not used in this analysis because it is assumed that there is no contamination in those particular soil samples. Possible reasons for this include (1) the contamination had evaporated, biodegraded, or migrated or (2) the soil sample location was outside the extent of the contamination.

There were three different samples where BZ was detected above the LDL and TPH was not detected for the same location and sample depth. A possible explanation is that Method 418.1 (the only method reported for TPH samples) does not accurately measure the lighter fractions of petroleum. Petroleum hydrocarbons, therefore, may have been present in these samples, but at levels below the LDL for TPH. Another possible explanation is that the detected BTEX constituents migrated to the sample location from petroleum contamination elsewhere in the soil. These reasons could explain the presence of BTEX in these three samples

BTEX to TPH Data. The forty-five BTEX to TPH calculated ratios were obtained from samples where the analytical method used to measure TPH concentrations detected TPH levels above the indicated LDL. Thirty-two separate instances were noted where neither TPH nor BTEX was detected in the same sample. These are not used in this analysis because it is assumed that there is no contamination in those particular soil samples. There were nine other instances identified where one or more of the BTEX compounds was detected above the analytical method LDL, but TPH was not detected from the same sample. Six of these nine cases, however, had no detection of BZ. The possible reasons for this are the same as previously discussed.

Table 20, below, identifies the distribution of the BZ to TPH and BTEX to TPH ratios calculated for JP-4 sites.

TABLE 20

RATIO DISTRIBUTION AT JP-4 SITES

(BZ/TPH)*100	Frequency	(BTEX/TPH)*100	Frequency
<0.5[a]	43	<4.52[b]	38
>=0.5	2	>=4.52	7
TPH=0, BZ > LDL	3	TPH = 0, BTEX > LDL	9[c]

[a]: average virgin JP-4 product BZ % of JP-4 obtained from the literature (see Table 21)

[b]: average virgin JP-4 product BTEX % of JP-4 obtained from the literature (see Table 21)

[c]: only 3 of the 9 have BZ > LDL

Statistical Analysis of Ratio Decline. The BZ to TPH and the BTEX to TPH ratios were analyzed statistically to determine whether or not the ratios identified from the JP-4 site data are statistically less than the average expected ratio from distilled, airplaneready JP-4. The goal of this analysis is to determine if the assumptions used in the California LUFT Guidance and by Stokman and Dime are appropriate for JP-4 contamination. In other words, the assumption that residual petroleum contaminated soil contains the same ratio of BZ and total BTEXs to TPH as found in pre-spilled JP-4 is evaluated.

Table 21 below shows the average BZ and BTEX concentrations used for this analysis as calculated from the JP-4 composition data identified from three sources in the literature. The researchers noted that the sources listed the same concentrations of BTEX found in JP-4. In other words, the variance was zero. Average JP-4 ratios were used because it was not possible to determine the actual constituent concentrations of the JP-4 for each site before it was spilled. Because the data does not identify when the site spills occurred, an analysis of the ratio decline over time was not conducted.

TABLE 21

AVERAGE BTEX CONCENTRATIONS FOUND IN JP-4

Constituent	Avg. Concentration by Weight (%)
Benzene	0.5
Toluene	1.33
Ethyl-Benzene	0.37
Total Xylenes	2.32
Total BTEX	4.52
	(1;2;20)

The Wilcoxin Signed-Rank Test was chosen to determine if the decline of the weathered product BTEX/TPH ratio is significant when compared to the virgin product ratio. For this test, the ratios calculated from the JP-4 sites are subtracted from the average virgin product ratio. These differences (δ) are then ranked in order of increasing magnitude (ignoring the sign of difference for the moment). In other words, the δ with the smallest magnitude is assigned a rank of "1" and the next highest magnitude is assigned a rank of "2", and so on. Duplicate in absolute magnitudes of the δ's are assigned the average of the ranks they would receive if they differed slightly from one another. The signs of the δ's are then restored to the rankings.

The test criterion is the sum of the positive rankings ($\underline{S}_+$). The null hypothesis for this test is that the median value of the calculated ratios from the JP-4 site data is the same as the average ratio expected from distilled JP-4. The alternative hypothesis is that the median value of the site ratios is less than the average JP-4 virgin product ratios. The shape of the frequency distribution of the site ratios need not be identified. The Wilcoxin Signed-Rank test, however, does assume a symmetric distribution. Under the null hypothesis, each rank is equally likely to be positive or negative, but under the alternate hypothesis, we expect more positive than negative differences. As a result, a large value of $\underline{S}_+$ is evidence to conclude the site ratios are less than the virgin product ratios (33:141-142).

The $\underline{S}_+$ value is then checked against the rejection region developed for the test. For this analysis, rejection regions for an α of 0.05 are used. An α at this level limits the probability of a Type I error to five percent. A Type I error for this analysis corresponds to deciding if the calculated JP-4 site data ratios are statistically less than virgin JP-4 product ratio when, in fact, they are not. Because the sample size for this analysis exceeds twenty ($\underline{n} > 20$), $\underline{S}_+$ has approximately a normal distribution (14:607). Since this is the case the large-sample test statistic is given by:

$$S_+ = Z_\alpha [\sigma_s + \mu_s] \qquad (1)$$

where Z_α is the 100(1-α) percentile from the standard deviation of the S_+ statistic, σ_s is the standard deviation of the S_+ statistic, and μ_s is the mean of the S_+ statistic. For example, for α equal to 0.05, the $P(Z < Z_{.05}) = .95$, where Z represents a standard normal random variable. The standard deviation and the mean are defined as follows:

$$\sigma_s = \sqrt{\frac{[n(n+1)(2n+1)]}{24}} \tag{2}$$

$$\mu_s = \frac{n(n+1)}{4} \tag{3}$$

where n is the number of samples (calculated ratios for this test).

The first application of this test is the analysis of sample BZ to TPH ratios. The cases where TPH was not detected and one or more of the BTEX components were detected are ignored. Because hydrocarbons are obviously present, yet not detected with the TPH analytical method, these cases are inappropriate for this analysis. Forty-five JP-4 samples were obtained and used for this test ($n = 45$). A Z_α value equal to 1.645 is used for this analysis to limit the probability of a Type I error to five percent ($Z_{0.05} = 1.645$). The null hypothesis (H_o) is that the δ's are 0. This null hypothesis assumes that the ratios at JP-4 sites are not statistically different from the average ratios identified for distilled JP-4. The alternative hypothesis (H_a) is that the δ's from the JP-4 sites are significantly greater than 0. In other words, the ratio declines. The null hypothesis is rejected in favor of the alternative hypothesis if the sum of the positive ranks (S_+) is greater than 663 which is calculated from equation (1) for $Z_{0.05} = 1.645$ and $n = 45$. The sum of the positive rankings ($\underline{S}_+$) for this case was 946. This $\underline{S}_+$ value is greater than 663 which results in rejection of H_o in favor of H_a.

The second application of this test includes the three cases where BZ was detected and TPH was not detected for the same sample. The validity of these samples is questionable because hydrocarbons are obviously present if benzene is detected. The authors believe that the discrepancy is a analytical methods issue and could be ignored for this analysis. These cases are, however, incorporated as worst case ratios and thus assigned the highest magnitude and negative ranks. The new number of samples is forty-eight which requires a modification of the rejection region $\underline{S}_+$ value. For this analysis the H_o rejection region is for calculated $\underline{S}_+$ values above 748. The $\underline{S}_+$ value calculated for this case is 946 which rejects H_o in favor of H_a. Table 22 below summarizes the statistical parameters used in the two applications of the Wilcoxin Signed-Rank Test for the BZ to TPH analysis.

TABLE 22

JP-4 SITE BZ TO TPH RATIO DECLINE TEST

Null hypothesis: H_o: $\delta = 0$		n = 45 (for first analysis) n = 48 (for second analysis)
Test statistic value:	S_+ = the sum of the ranks associated with positive δ	
Standard Normal value:	$Z_\alpha = 1.645$	
Type I error value:	$\alpha = 0.05$	
Alternative hypothesis H_a: $\delta > 0$		Rejection region for level alpha test $S_+ >= 663$ (for first analysis) $S_+ >= 748$ (for second analysis)

The BTEX to TPH ratio decline test statistic is the same as the BZ to TPH ratio decline test. For the initial analysis, the cases where TPH was not detected and one or more of the BTEX components was detected are ignored. The number of ratios obtained from the data and used for this test is forty-five (n = 45). The null hypothesis (H_o), the alternative hypothesis (H_a), and $\underline{Z}_{\alpha}$ are the same for this analysis as the BZ to TPH analysis. The null hypothesis is rejected in favor of the alternative hypothesis if the $\underline{S}_{+}$ is greater than 663. The $\underline{S}_{+}$ value determined for this case is 780 which rejects H_o in favor of H_a.

The second application of this test includes the cases where BTEX was detected and TPH was not detected for the same sample. Like the BZ to TPH analysis, the validity of these samples is questionable because hydrocarbons are obviously present if BTEXs are detected. The authors believe that the discrepancy is a analytical methods issue and could be ignored for this analysis. These cases are, however, incorporated as worst case and thus assigned the highest negative ranks. It is important to note that for these nine cases BZ was detected only three times. The new sample number is 54 which changes the rejection region $\underline{S}_{+}$ value. For this analysis the H_o rejection region is for $\underline{S}_{+}$ values greater than 933. The $\underline{S}_{+}$ value determined for this case is 780. Because $\underline{S}_{+}$ is less than 933, the null hypothesis is not rejected at the 95% confidence level. Table 23 below summarizes the statistical parameters for the two applications of the Wilcoxin Signed-Rank Test for the BTEX to TPH analysis.

TABLE 23

JP-4 SITE BTEX TO TPH RATIO DECLINE TEST

Null hypothesis: $H_0: \delta = 0$

$n = 45$ (for first analysis)
$n = 54$ (for second analysis)

Test statistic value: S_+ = the sum of the ranks associated with positive δ's

Standard Normal value: $Z_\alpha = 1.645$

Type I error value: $\alpha = 0.05$

Alternative hypothesis
$H_a: \delta > 0$

Rejection region for level alpha test
$S_+ >= 663$ (for first analysis)
$S_+ >= 933$ (for second analysis)

Cost Savings

As stated in Chapter III, the IRPIMS database contains approximately 60% of all the sample information taken as a result of Air Force IRP efforts. It is important to note that subsequent data has been added to IRPIMS since the data used for this research was extracted. From the IRPIMS data analysis, an estimate is made of the percentage of Air Force petroleum sites that would require remediation under a TPH standard and the percentage of sites that would require remediation under a BTEX standard. From these estimates, the researchers calculate a range of cost savings that could result if a BTEX based standard is applied to all Air Force petroleum sites.

Sites with Contamination Exceeding 100 ppm TPH. Sixty-six of the 120 identified petroleum contaminated soil sites have contamination exceeding 100 ppm TPH. As stated in Chapter III and identified in Chapter IV, 100 ppm TPH is used in this analysis because it appears the most often as a recommended cleanup level by states that use TPH as a cleanup parameter for petroleum contamination. The researchers believe that the IRPIMS data is representative of all Air Force sites. In other words, of the known petroleum sites in IRPIMS, 55% have one or more TPH samples where the contamination exceeds 100 ppm. The assumption is made, therefore, that 55% of all Air Force petroleum contaminated soil sites would require cleanup action under a cleanup standard of 100 ppm TPH.

Sites with Contamination Exceeding 10 ppm BTEX. Sixteen of 120 identified petroleum sites have contamination exceeding 10 ppm total BTEX. As identified in Chapter IV, 10 ppm total BTEX is used because it is the most common cleanup level used by states for BTEX. Analysis of the data shows that only 13% of all Air Force petroleum contaminated soil sites would require cleanup action under a cleanup standard of 10 ppm total BTEX.

Estimate of Air Force Cost Savings. From the estimated 87% of Air Force petroleum contaminated sites that would not require cleanup under a BTEX standard, an estimate of cost savings in dollars can be made. According to Miller, 60% of the 4,400 Air Force hazardous waste contaminated sites (or 2,640 sites) are contaminated with petroleum. .Miller also estimates that the cleanup costs for each petroleum contaminated site could range from $100 thousand to $1 million. A simple calculation (percentage of sites not requiring cleanup under a BTEX standard, multiplied by 2,640 sites, multiplied by $100 thousand to $1 million) shows a potential savings in the range of $230 million to $2.3 billion. This estimate provides an indication of the magnitude of savings which may result from the successful negotiation of a BTEX standard at Air Force petroleum contaminated sites.

Conclusions

The results of this analysis clearly indicate that the BZ and total BTEX constituents in JP-4 are preferentially weathered when compared to all petroleum hydrocarbons comprising JP-4. This analysis also shows that the IRPIMS data is limited for certain analyses. From a cleanup cost perspective, the IRPIMS data analysis indicates there is potential for substantial savings if cleanup of petroleum sites were based on a BTEX standard.

First, the ratios of BZ to TPH and BTEX to TPH obtained from the data are significantly less than the average ratio expected from pre-spilled JP-4 in all but one case. For three out of the four tests, the analyses indicate a decline in the BZ and the total BTEX components at weathered sites with confidence exceeding 95%. This is significant because the results show that the residual soil concentration assumptions used in the California LUFT Guidance and by Stokman and Dime are inappropriate for JP-4 soil contamination. Therefore, the assumptions are overly-conservative for BTEX. The analysis also shows, however, that in the BTEX worst case test (where one or more of the BTEXs were detected but TPH was not detected for the same sample), that it cannot be stated with 95% confidence that the BTEX constituents weather faster than all measured JP-4 petroleum hydrocarbons. The statement can be made however, with 63% confidence, that the BTEX constituents weather faster than measured petroleum hydrocarbons. It is not plausible, however, to have BTEX and no TPH measured from the same sample. Because of this, the samples where BTEX was detected and TPH was not detected could be ignored and thus satisfy the 95% confidence level.

Second, the information contained in the IRPIMS database is not sufficient to allow an analysis of the relationship of BTEX to TPH over time or for varying hydrogeological site conditions. It should be noted, however, that Air Force Installation Restoration Program data is continually being added to IRPIMS which may result in a successful analysis of this nature in the future.

Lastly, the IRPIMS data shows that 76% fewer petroleum sites would require action under a BTEX cleanup standard as opposed to a TPH standard. Successful negotiation of a BZ or BTEX cleanup standard by Air Force remedial project managers could save the Air Force substantial dollars in cleanup costs and the tracking costs associated with active sites. And, because the data shows that the BTEX aromatics weather faster than the measured total hydrocarbons, the cleanup time required for these sites, using Bioventing or similar remedial technologies, could be significantly less than the time it would take if site cleanup were based on a TPH standard.

The following chapter concludes the research process with a project summary, a statement of significant findings, the significance of the research, and recommendations for further study.

VII. Conclusions and Recommendations

Project Summary

Previous research addressing petroleum contaminated soil cleanup standards identifies the inconsistencies that exist in such standards. Research focusing on the use of "total petroleum hydrocarbons," however, is limited. The need for a detailed evaluation of the use of TPH as a cleanup standard has been supported by Air Force officials at the Air Force Center for Environmental Excellence and by members of the Council for the Health and Safety of Soils (CHESS). This research fulfills this need.

To evaluate the TPH standard for cleanup of petroleum contaminated sites, four research objectives were investigated and answered. The objectives included (1) characterizing and explaining current cleanup standards for petroleum contaminated soils, (2) comparing the application of a TPH standard against a BTEX (benzene, toluene, ethyl benzene, and xylene) standard, (3) investigating the relationship of BTEX to TPH in soil at petroleum contaminated sites, and (4) estimating potential cost savings associated with the use of a BTEX based cleanup standard verses a TPH based standard.

The evaluation of the use of TPH as a cleanup standard was performed through a review of the literature, analysis of state standards, interviews with state regulators and technical experts, and an analysis of data contained in the Installation Restoration Program Information Management Systems (IRPIMS). The significant findings are presented below.

Statement of Significant Findings

Analysis of State Standards. An analysis of state standards was performed to characterize current cleanup standards used for cleanup of petroleum hydrocarbons. From this analysis, a substantial variation can be seen in the standards used for cleanup of petroleum contaminated soils. TPH is the most commonly used parameter for cleanup of petroleum contaminated soils. Compound specific standards, however, are accepted and required by several states.

For gasoline, MTBE is the only commonly used indicator compound, other than BTEX and TPH, for which states have set standards. Naphthalene and polynuclear aromatic hydrocarbons are the only indicator compounds, other than BTEX and TPH, commonly used by states for diesel. Chapter IV provides an analysis of other indicator compounds used for gasoline and diesel. This list may be used to identify compounds, other than BTEX, which might be considered for a compound specific standard.

<u>Evaluation of the Use of a TPH versus BTEX Cleanup Standard</u>. Although several sources in the literature state that TPH should be used only for screening, state regulators and technical experts report that TPH is, in fact, used for making risk based cleanup determinations. The regulators and experts provide many advantages which support the use of TPH for both screening and as a cleanup standard. In addition, studies such as the California LUFT manual and Stokman and Dime research conclude, using questionable assumptions, that soil contaminated with 100 ppm TPH will not present risk to groundwater or human health. These studies, however, are cited by states and technical experts as part or all of the basis for state standards. These findings contribute to and explain the popularity of a TPH based cleanup standard.

The one significant drawback of TPH, as stated in the literature and mentioned by state regulators and technical experts, is that a TPH standard is overly conservative and can drive unnecessary cleanups. The analysis of Air Force data maintained in IRPIMS demonstrated that the use of a 100 ppm TPH cleanup standard may be overly conservative because BTEX was shown to be preferentially weathered over TPH with time in JP-4 contaminated soils. The researchers hypothesize that the same conclusion is true for other types of petroleum products. Further analysis of IRPIMS information demonstrated that a strict 100 ppm TPH cleanup standard might drive soil cleanup for a significant number of sites (55%), yet under a strict BTEX based standard only 13% would require cleanup. These findings highlight the need to identify the appropriate cleanup standard when addressing petroleum contamination.

A compound specific standard is one alternative to a cleanup standard based on TPH. It is shown in the analysis of state standards that some states use a compound specific standard for cleanup of petroleum contaminated soils. As demonstrated, the use of a BTEX based standard focuses on those constituents likely to contaminate groundwater and has the potential to reduce cleanup costs due to preferential weathering of the BTEX constituents.

Interviews with state regulators indicate that states have the flexibility in their regulations to use a compound specific standard. States also indicate, however, that in order to justify contamination which exceeds recommended cleanup levels, responsible parties must either meet state specific cleanup criteria or conduct site specific risk assessments to justify less restrictive cleanup goals. Therefore, based on the sample interviewed, provisions for flexibility exist but the ultimate approval is made by individual state regulators.

A significant finding from these interviews, however, is that many interviewees are not comfortable using a compound specific standard without an accompanying analysis for TPH. The most frequently expressed concern is that a compound specific standard ignores the hundreds of other petroleum hydrocarbons in the soil. Specifically, the lack of toxicological and fate and transport information about these remaining hydrocarbons yields concern whether or not the remaining constituents present risk to human health via soil ingestion or contamination of the groundwater.

The literature review shows that a gap exists in our current understanding of the toxicity of longer chained hydrocarbons. Information does exist, however, which indicates that the longer chained hydrocarbon fractions of petroleum are not as mobile as the shorter chained BTEX compounds. Even though studies exist which demonstrate the low mobility and low potential the longer chained hydrocarbons have for contaminating groundwater, the perception by regulators that these compounds might present risk to groundwater will most likely be a challenge to proponents of a compound specific standard.

Relationship of BTEX to TPH over Time. Based on BTEX and TPH soil sample data contained in the IRPIMS database, this research has demonstrated that the ratio of BTEX to TPH declines with time. These results indicate that the constant ratio of BTEX to TPH assumed by the California LUFT manual and Stokman and Dime's research is not valid. A conclusion can be made, therefore, that these studies use an overly conservative estimate of soil TPH levels which are protective of groundwater and human health.

This work demonstrates, based on actual field sampling data, what researchers have hypothesized intuitively: BTEX in soil contaminated with petroleum is preferentially weathered with time as compared to the total petroleum hydrocarbons.

Analysis of Cost Savings. This research identifies the relative cost savings that would result if a BTEX based standard, instead of a TPH standard, were required at all Air Force petroleum contaminated sites. The calculation of savings is made using sampling data from IRPIMS. Based on 120 identified petroleum sites contained in IRPIMS, 66 of which have TPH concentrations above 100 ppm, this research shows that only 13% of those sites would require cleanup under a 10 ppm BTEX standard. Considering the IRPIMS data to be representative of all Air Force sites, the findings indicate that 87% of all Air Force petroleum contaminated soil sites would not require cleanup action under a BTEX based standard. This could result in dollar savings ranging from $230 million to $2.3 billion.

Recommendations

A compound specific cleanup standard should be considered for both gasoline and diesel. Site managers should consider justifying leaving petroleum contamination in the ground, with levels of TPH exceeding 100 ppm, if the following conditions are present: (1) mobile and risk based BTEX compounds are not present, and (2) soil ingestion is not a concern. To justify leaving diesel contamination in the ground, in excess of 100 ppm TPH, the responsible party must convince regulators that the risk associated with the longer chained hydrocarbons and multi-ringed hydrocarbons, including naphthalene and other PNA's found in diesel, does not exist because of their low mobility and low potential to contaminate groundwater.

Significance of Research

The analysis of the relationship of BTEX to TPH in petroleum contaminated soils provides evidence that BTEX is preferentially weathered over TPH. This finding clearly indicates that the assumptions used in the studies upon which current soil cleanup standards for petroleum are based are overly conservative. These results may be used by site managers to negotiate site cleanup standards based on either compound specific indicators or higher TPH levels. The analysis of cost savings which would result from the use of a BTEX standard is also significant. These findings may also be used by site managers for negotiating site cleanups.

This research characterizes state regulatory viewpoints on the application of both TPH and compound specific standards for soil cleanup. Because previous surveys have focused only on the nature of state cleanup standards and have not characterized regulatory viewpoints, this is the only survey of its kind that exists. The survey conducted also characterizes the flexibility and use of risk assessments by state regulators, which has not been done before.

Finally, the Air Force has an initiative to develop and justify a health-based cleanup standard for petroleum contaminated soils. The information provided here will assist the Air Force in formulating a position to address the regulatory concerns in accepting compound specific cleanup indicators for making cleanup determinations.

Recommendations for Further Study

As a part of this research, twenty-five percent of the state regulators were interviewed. This sample was adequate and appropriate for characterizing the viewpoints requested during the survey. Room exists, however, for additional work in this area. First, with the information provided in this study, a more in-depth survey questionnaire could be developed which contains quantitative questions. Second, all fifty states could be interviewed to obtain a complete summary of regulatory perspectives.

Because adequate data did not exist to enable the researchers to evaluate the relationship of BTEX to TPH over time and hydrogeological site conditions, this is another area for further research. The type of data necessary to perform such as study may be present in other sources. These sources include: (1) Air Force data not yet entered into IRPIMS, (2) databases maintained by other organizations such as the Army Corps of Engineers, and (3) results of cleanup investigations at both government and private sector petroleum contaminated sites.

Similarly, another area for recommended research is actual field tests (in-situ) to determine the relationship between BTEX and TPH over time and varying hydrogeological and geochemical field conditions. Experiments would be conducted using petroleum for which the exact chemical composition is known. Defined plots of soil would be contaminated with this petroleum, and measurements of specific compounds could be taken over time. Through this type of study, the actual weathering rate could be calculated as a function of time. Different plots of soil could be established with varying soil types, soil pH, organic carbon content, and other hydrogeological and geochemical variations. By isolating each variable condition, the weathering of petroleum, as a function of each variable could be calculated. This type of study would establish a better understanding to the scientific community of the relationship between BTEX and TPH.

Additional work might also be conducted in analyzing the information contained in IRPIMS. Much groundwater data from petroleum contaminated sites exist which might be used to establish general correlation between contaminant levels in groundwater and contaminant levels in soil for petroleum contaminated sites. This type of analysis might provide information on the migration of BTEX from contaminated soil to groundwater. Furthermore, IRPIMS could be analyzed to evaluate the concentrations of other chemical compounds present at petroleum contaminated sites.

State Regulator Interview: Delaware

7 May 93

Contact: Pat Ellis
Hydrologist
DE Department of Natural Resources and Environmental Control
Underground Storage Tank Branch
LUFT investigation and corrective action

2. What Cleanup standards and guidelines are currently used by your state for cleanup of PCSs and groundwater?

a. Distinguish between action levels and cleanup levels for each type of petroleum product regulated.

- Notification level: "any release". Soils magazine reports detection limits (minimum laboratory detection). When tanks are removed, parties must submit results no matter what they are, agency determines if anything needs to be done.

- Action level: department has certain set numbers used for different site categories.

High risk "A" Sites: resource protection area or watershed area within a certain distance of public or domestic wells or surface water bodies, or groundwater less than five feet. [Action level criteria are more stringent than for sites in Category B and will be determined on a site by site basis by the Department after its evaluation of site characteristics, perceived risks, and anticipated effectiveness of various remediation options.]

Medium risk "B" Sites: most sites, moderate risk. Further from domestic wells or nobody using domestic wells in the area. Six to eight criteria used (will send further information). Action levels are:

- 100 ppm TPH or 10 ppm BTEX for gasoline, kerosene, jet fuels
- 1000 ppm diesel, heating oils, waste oils (and 10 ppm BTEX)
- If exceed either of these, then must investigate site

Low risk "C". Industrial areas. Category not used very much. Sites far from wells. Action level for these sites is less stringent than for sites in Category B. [The Department will make the determination on a site-specific basis after evaluating site characteristics, perceived risks, and anticipated effectiveness of various remediation options.]

- Cleanup levels: there are no specific cleanup levels. Closure guidelines say that they should be less than action levels. Action levels are all soil numbers. There are no action levels for groundwater. For soil cleanup try to get below action levels.

b. Are your cleanup levels flexible? Why or why not?

- No defined standards for cleanup or investigation for groundwater. There never have been any. In some areas will let someone get away with 10 ppm BTEX in groundwater, sometimes 1 ppm, other times go down close to drinking water standards. It's all risk based.

- Action levels are for soils only. If department thinks there is a problem with the number, department is flexible. Reserves the last decision in categorizing sites into category A,B or C. Regulations include the phrase "other department defined criteria", based on the decision of the department. Department is always willing to listen to what guy has to say as to why he has put a different risk status on a site or what he thinks the cleanup level should be.

c. Is risk assessment required for cleanup of PCS? If so, when?

- risk based approach, site investigation is required if action levels are exceeded

- sites are categorized according to sensitivity. Department categorizes into levels A, B, and C based on risk and possible impact to things in the area. Classified into one of three categories, then look at action levels and see where the sample results fall with respect to action levels. If action levels are exceeded, will go either to a limited investigation which can be a couple of soil borings down to the depths of the tanks or a couple of feet below, or more detailed investigation.

d. If risk assessment is used, does your state consider TPH levels in assessing risk? If so, in what respect? If not, why?

- Yes. If either BTEX or TPH is above the action levels investigation is required. In the cleanup, the department tries to get them both down below the action levels.

- Use both BTEX and TPH in the remediation, corrective action phase. More concerned about the BTEX. More flexibility with the TPH. Very site specific. No definite answer, frustrates consultants to no end. After they do an investigation they are never sure whether the department will require cleanup or will allow monitoring. State has flexibility to look at a site for impacts... looking at sensitive receptors, surface water, subsurface water, vapors into basic. It is a risk assessment for every site.

e. How does your state regulate soils contaminated with jet fuel?

- Regulated the same as gasoline and kerosene.

f. Does site age make a difference in how PCS is regulated?

- Not a lot. It might be considered and taken into account during the assessment of risk.

g. Does your state have plans to change the standards? (Describe)

- About a year ago, looked at changing the standard. Will want to look at it in the future.

3. Please explain the rationale behind the development of your state's current cleanup standard.

- Believe the standards were derived from NJ standards.

4. Please present advantages and disadvantages in using a TPH cleanup standard.

- I know one thing, we probably do not want to drop the TPH because we have frequently found that you will remove a tank and get the soil sample results and have acceptable, a little bit above the action level TPH levels and step out and you'll find the BTEX! It's gone a little farther. I found one that went from non-detect to 1000 ppm in less than 10 feet. The TPH had been 120 ppm, though step out a few feet, the TPH will go away or below the action levels, and we'll be fine. Found out that the TPH did not change a bit, but the BTEX jumped to over 1000 ppm. Jumped out another twenty feet, found 50-60 ppm in the groundwater and occasionally free product.

- Problem with not finding BTEX, never quite sure until you've looked farther about where it went. Has it degraded, volatilized or gone down into the groundwater?

- Of the many chemicals that show up in TPH, there are many that present risk to human health. State has not looked at specific compounds within TPH other than BTEX.

- TPH is used by the Department as an indicator, but likes to see soil with measured TPH levels cleaned up as well.

- [For indicating contaminate mobility]: TPH is the less mobile fraction. If have gasoline, BTEX is going to move, but TPH is an indicator of what else is there. If have TPH contaminated soil without BTEX, could have a long release over a long period of time [of BTEX] with the other hydrocarbons left as a residual.

5. If a TPH cleanup standard is used, are different cleanup levels appropriate for different petroleum products (i.e. gasoline vs diesel).

- Yes. TPH from gasoline may mean more mobile phase somewhere else, and may mean a long release over a long period of time. With the heating oils and diesel, they do not have the volatile component, and TPH analysis represents close to 100% of what is in those fuels. Therefore, could have a smaller release and have a good size number.

6. Please present advantages and disadvantages associated with using a compound specific standard.

- "For cleanup, more worried about the BTEX based on health". Most concerned about BTEX, plus its more of the earlier warning indicator, it moves farther.
- Sometimes seen TPH and no BTEX, go a little farther and find out where the BTEX has gone.

- Disadvantages: not many.

7. If a compound specific standard is used, what chemical compounds should be included (identify for different petroleum products)?

- Department doesn't usually see TPH broken down, but naphthalene and benzo(a)pyrene would be considered. MTBE might also be considered as an early warning indicator.

State Regulator Interview: Illinois

24 May 93

Contact: Dr. Tom Hornshaw
Manager, Toxicity Assessment Unit
(Environmental Protection Specialist)
Office of Chemical Safety
Illinois Environmental Protection Agency
- Helped establish state soil standards (and objectives)

2. What cleanup standards and guidelines are currently used by your state for cleanup of PCSs and groundwater?

- See levels given in Soils magazine

- These are not standards. Standards carry the weight of law and can be enforced. Thus, levels given for soil are objectives. Objectives are levels required to get an "all clean" letter from the state.

a. Distinguish between action levels and cleanup levels for each type of petroleum product regulated.

Action Levels: any detection triggers a site into the program

Cleanup Levels: levels at which the state accepts as "clean". No further requirements will be applied for soils meeting these levels. Therefore, the property can be sold, etc.

b. Are your cleanup levels flexible? Why or why not?

- Yes. Two processes can be used. (1) Show site has minimal impact, or potential impact, on groundwater. The site will be held to a slightly less stringent cleanup standard than the established cleanup levels. (2) Conduct site specific cleanup determination which goes through a risk management group within the agency. Group can accept as clean (no further cleanup required) sites with extenuating circumstances. Examples include further cleanup which: (1) would damage the integrity of buildings or existing utility lines, (2) is too costly, (3) is physically not do-able because of excavation requirements or limits of equipment have been reached, etc.

c. Is risk assessment required for cleanup of PCS? If so, when?

- Not required but can be performed for site specific cleanup determinations.

d. If risk assessment is used, does your state consider TPH levels in assessing risk? If so, in what respect? If not, why?

- State has looked into this on several different occasions, and every time they looked at it, it seemed to be a bad idea because of problems with false negatives and false positives, interferences from natural hydrocarbons, high enough detection limits that you don't see the chemicals of concern (especially benzene), and several other problems, both analytical and technical.

- Not sure if TPH concentrations are looked at by the risk management group when evaluating risk

e. How does your state regulate soils contaminated with jet fuel?

- As a middle distillate fuel (see standards in soil magazine)

f. Does site age make a difference in how PCS is regulated?

- No

g. Does your state have plans to change the standards? (Describe)

- Not sure. There has been some "noise" from petroleum marketers and the Chamber of Commerce to get a legislative cleanup level to replace the states current levels. Not sure where this is at this point.

3. Please explain the rationale behind the development of your state's current cleanup standards?

a. What is the technical basis for the standards?

- Cleanup levels were derived from either groundwater quality standards or groundwater health advisories.

- Used a very conservative estimate of how much contamination can be left in soil in order to never present a threat to groundwater. In the case of chemicals that are mobile in soil, such as BTEX, a simplifying assumption was made that all of the chemical can show up at the groundwater interface, undiluted. No type of dilution attenuation factor is used. The groundwater quality standard was used with the units changed from mg/l to mg/kg which became the soil cleanup objective.

- For other chemicals that are not mobile in soil, such as the PAH's, the state used a twenty fold dilution attenuation factor (i.e. multiply the groundwater standard by twenty), and changed the units to mg/kg. This became the soil objective for these chemicals.

- To determine mobility in soil, state uses ethyl benzene as the cutoff chemical. Through experience they've seen where ethyl benzene is present in both soil and groundwater, and they're pretty sure of its mobility potential. They use the organic carbon partition coefficient (KOC) of ethyl benzene as the cutoff for what is mobile and what is not mobile.

- Use BTEX and 16 priority PAHs as indicator compounds (for the most part). If cleanup is performed to the cleanup objectives, state feels confident that if these objectives are met, TICs and other unknowns will be cleaned up as well. This is another advantage of a chemical specific standard.

b. Was another state's approach (or specific study) used in establishing your standards (i.e. California LUFT manual or Stokeman & Dime's research)?

- State looked at these studies, but did not model their standards after them.

4. Please present advantages and disadvantages in using a TPH cleanup standard.

Advantages: quick, easy, and cheap.

Disadvantages: false negatives and false positives. Detection limit is such that it cannot be guaranteed that benzene left in the soil will be at levels protective of groundwater.

- Not sure how well TPH concentrations associate with PAH levels in the soil. States cleanup levels for PAHs (carcinogenic) are in low ppb range. A TPH standard will probably not remove PAHs to these levels.

- It's possible that the petroleum marketers want TPH as a standard. Previously, the marketers were all for a TPH standard. Their own consultants told them, however, that in some cases they will be in trouble because of naturally occurring organics and also because TPH detection can be fooled by fine particulates. It's possible to have soil with no hydrocarbons, but fine particulates can be read as if they were hydrocarbons (thinks IR detector is the problem).

5. If a TPH cleanup standard is used, are different cleanup levels appropriate for different petroleum products (i.e. gasoline vs diesel).

- N/A

6. Please present advantages and disadvantages associated with using a compound specific standard (address risk and mobility considerations).

Advantage: fairly good confidence that there will never be any groundwater problems if soil objectives are met. This is probably the big advantage.

- IL's standard probably drives more cleanup. Evidence of this fact is the petroleum marketers going to the legislature to have the standards changed. Mr. Hornshaw is not sure whether they want TPH, but they want a standard less strict and faster than Illinois's current standards.

- A lot of station owners and petroleum marketing people think that the state is too conservative. IL has actually done some computer modelling (using the SESOIL model used by EPA), and varied a lot of the parameters such as the depth to groundwater, soil types, porosities, etc. In worst case situations, even at the fairly stringent cleanup levels used by IL, the studies show that there can be temporary exceedences of the groundwater quality standards (for benzene for instance). They've done enough modelling to convince themselves that in some cases the benzene standard in groundwater can be exceeded by leaving 5 ppb benzene in the soil. It's a function of the total depth of the contamination, distance to groundwater, soil type, and volatilization rates.

- State is fairly convinced they are on the right track as far as cleanup levels. It is up to the state legislature at this point (whether they will side with the state or side with the petroleum marketers).

- State has experienced a couple of really old LUST sites with a petroleum odor in the soil, but good analytical data that showed no BTEX, PAHs or lead. (Mr. Hornshaw believes) state decided that site was clean enough. There has only been a couple of sites like this, however, so there has not been much of a track record to go on.

7. If a compound specific standard is used, what chemical compounds should be included (identify for different petroleum products)?

- N/A (see list in Soils magazine)

8. Is there any other information/considerations you would recommend we look at in our research?

- Do not know of any off-hand.

State Regulator Interview: Kentucky

25 May 93

Contact: Mr. Doyle Mills
Manager, Underground Storage Tank Branch
Kentucky Department for Environmental Protection
- Worked with petroleum/solvent contaminated soils for 12 years in UST of state Superfund program
Ph: (502) 564-2705

2. What cleanup standards and guidelines are currently used by your state for cleanup of PCSs and groundwater?

- PIDs and FIDs are used in the field. Only when the PID registers below 50 or 100 (whatever they are comfortable with) then they send a sample off for laboratory analysis. Consultants use this to correspond to the states cleanup levels. One consultant consistently uses 50 ppm (anything below 50 ppm he'll send for laboratory analysis) and analysis almost always shows less than 1 ppm BTEX.

a. Distinguish between action levels and cleanup levels for each type of petroleum product regulated.

- Action levels are the same as cleanup levels. Options for site with soil above the levels listed below include: (1) removal, (2) treatment in-situ, (3) leaving the soil in place (if cannot be feasibly removed such as if it is under a building), or (4) conducting a risk assessment.

Gasoline, kerosine, jet fuel:	1 ppm BTEX
Diesel:	1 ppm PAH
Waste Oils and Lubricating Oils:	10 ppm Oil & Grease *

* Oil & Grease method for soil is 3540/3550 extraction method with 9071 for analytical method - measures heavier fractions of oil and grease)

- Groundwater cleanup levels:

5 ppb BTEX and PAHs
5 ppm oil and grease (by SW846)

b. Are your cleanup levels flexible? Why or why not?

- Yes, if a risk assessment is performed, these levels are not strictly enforced. However, a risk assessment may show that soil must be cleaned up to levels lower than the established cleanup levels. This is one risk of performing a risk assessment.

c. Is risk assessment required for cleanup of PCS? If so, when?

- Not required, but allowed.

d. If risk assessment is used, does your state consider TPH levels in assessing risk? If so, in what respect? If not, why?

- State does not use TPH levels for assessing risk. Analysis must be compound specific.

e. How does your state regulate soils contaminated with jet fuel?

- Same as gasoline.

f. Does site age make a difference in how PCS is regulated?

- No. The only difference site age makes is lower levels of benzene and higher levels of xylene (percentage wise).

- According to Mr. Mills, from older sites he's seen (or will run into), if the site is really old, odds are that the levels of contamination [BTEX] will be pretty close to background. You will run into difficulties, however, if contamination is from waste oil.

g. Does your state have plans to change the standards? (Describe)

- There is a group headed by the University of Kentucky who is looking at the standards. Don't know at this time if they will recommend change.

3. Please explain the rationale behind the development of your state's current cleanup standards?

a. What is the technical basis for the standards?

- Standards were set based on detection limits of BTEX/PAHs/oil and grease
- Standards were developed using a risk assessment from the technical assistance section.
- Groundwater and public health concerns were used

- Soil cleanup standards were based on compounds that the state was interested in. Chemicals that were not chemicals of concern where not looked at in establishing the soil standards.

b. Was another state's approach (or specific study) used in establishing your standards (i.e. California LUFT manual or Stokeman & Dime's research)?

- In establishing KY's standards, other approaches were looked at and discarded. They were not that useful. Many studies looked at only one exposure pathway and did not look at some of the other more important pathways. Others only looked at public health and didn't look at impact on groundwater.

4. Please present advantages and disadvantages in using a TPH cleanup standard.

- Disadvantages:

(a). TPH doesn't tell you what you are measuring. All you have is a lump sum number that can be just about anything.

(b). TPH cannot be used to evaluate BTEX concentrations unless "wild" assumptions are used in estimating BTEX percentages in the TPH measurement (i.e. 5, 15, 20% BTEX etc). Kentucky's risk assessment personnel will not even look at TPH numbers generated. They require compound specific numbers.

- **[Can you think of any situations where you would have TPH concentrations in the soil and no BTEX?]** Yes, but according to Kentucky state's risk assessment experts, TPH will result from waxes and paraffins. These do not present risk and KY does not worry about them.

- Ran into situation where something was present in the water that did not show up as BTEX or PAH. They requested an extended 8100 method be run to pick up the longer chain hydrocarbons, This method will detect the "grease" type hydrocarbons. Risk assessment personnel said "not to bother" with these longer hydrocarbons.

6. Please present advantages and disadvantages associated with using a compound specific standard (address risk and mobility considerations).

Advantages: you know exactly how much BTEX is present. Can base risk assessment on real numbers.

7. [Do you know if the people that are looking at the standards are looking at any other chemical compounds, to be included?]

- No, they pretty much agree with the current list (BTEX, PAHs and oil and grease for waste oils.

State Regulator Interview: North Dakota

Date of Interview: 6 May 93
& 16 Jun 93

Contacts:
Mr. Mark Mittelsteadt
Environmental Engineer
ND State Dept. of Health
Division of Hazardous Waste Mgmt

Mr. Martin Schock
Environmental Engineer
ND State Dept. of Health
Environmental Health Section

Mr. Gary Berreth
UST Program Coordinator
ND State Dept. of Health
Division of Hazardous Waste Mgmt

1. Please state your name, title, and agency. Please describe your expertise and experience in regulating Petroleum Contaminated Soils (PCSs).

EXPERIENCE:

- Employed with the Underground Storage Tank Program for about 2 1/2 yrs.

- Duties include: inspection of underground tank removals, oversees soil removal activities at sites, review site investigation reports.

2. What cleanup standards and guidelines are currently used by your state for cleanup of PCSs and groundwater?

SOIL:

- We have a "recommended action level" (RAL) of 100 ppm TPH for petroleum contaminated soils

- This RAL of 100 ppm TPH was adopted in ND about three yrs ago.

GW:

- We have a RAL of 5 ppb benzene and 500 ppb TPH for groundwater. (The groundwater standards are set by the Division of Water Quality.)

- These levels apply to (for both soil and GW)...
  - -- motor fuels
  - -- jet fuels
  - -- distillate fuel oils (diesel, gasoline, etc)

-- residual fuel oils
-- lubricants
-- petroleum solvents
-- used oils

- For the most part, cleanup is site specific.

a. Distinguish between action levels and cleanup levels for each type of petroleum product regulated.

- Recommended action levels are levels, if exceeded, where ND may require further action. The criterion that we look to determine what further action is necessary is outlined in ND's "Cleanup Action level Guidelines for Gasoline and other Petroleum Hydrocarbons". **[see 2c. below]**

b. Are your cleanup levels flexible? Why or why not?

- What we require for action is flexible. Our cleanup decisions are on a site-by-site basis. [see 2c. below for criterion]

c. Is risk assessment required for cleanup of PCS? If so, when?

- ND does not have anything written as far as risk assessment is concerned (as it applies to soil cleanup).

- We look at each site on a case by case basis. "Under all circumstances, cleanup decisions are made on a site-by-site basis and take into consideration the nature of the release and the site." All decisions include the following factors: [the following info was extracted from ND's "Cleanup Action level Guidelines for Gasoline and other Petroleum Hydrocarbons" (pg. 1), sent by Mr. Mark Mittelsteadt]

(1) location of the site in relation to surrounding population
(2) the presence of free product
(3) the presence and proximity of municipal utilities
(4) the potential for migration of vapors
(5) the hydrogeology of the site and groundwater use
(6) the use and location of wells potentially affected by the release
(7) the future site use

- In the event of contamination above the RAL, we normally require a "site assessment plan" from the responsible party which addresses the above criterion. Usually consultants prepare the "site assessment plan" for the responsible party.

- We require the responsible party to develop a "cleanup action plan" for our approval before cleanup actions are taken.

d. If risk assessment is used, does your state consider TPH levels in assessing risk? If so, in what respect? If not, why?

- N/A

e. How does your state regulate soils contaminated with jet fuel?

- Again, we use 100 ppm TPH as an "action level" for all petroleum contamination.

f. Does site age make a difference in how PCS is regulated?

- Not normally.

g. Does your state have plans to change the standards? (Describe)

- Not aware of any plans to change our levels.

3. Please explain the rationale behind the development of your state's current cleanup standards?

- I believe ND looked at other state's soil cleanup requirements and based the 100 ppm TPH RAL on that.

[Is your state's soil cleanup standard connected to your state's GW standard?]

- I do not know of a connection, but you may want to check with the division of Water Quality.

a. What is the technical basis for the standards?

- I do not know of any.

b. Was another state's approach (or specific study) used in establishing your standards (i.e. California LUFT manual or Stokeman & Dime's research)?

- We looked at what other states were doing at the time we established our "action level". We looked at a published state survey on petroleum cleanup standards (may have been Dr. Kostecki's survey but not sure).

4. Please present advantages and disadvantages in using a TPH cleanup standard.

ADVANTAGES:

- You have standard laboratory methodology procedures available.

- With a TPH standard is that you are looking at the entire range of petroleum compounds as opposed to just BTEX. If you use just BTEX for your cleanup standard...you'll possibly be leaving behind some of the heavier fractions.

- [Mr. Barreth] TPH gives a target--a number that you can shoot for in cleaning up sites

DISADVANTAGES:

- [Mr. Barreth] "I do not think that the TPH analytical procedure is necessarily representative of the contamination that is in the soil."

- [Mr. Barreth] So much is dependent on the analytical technique and the nature of the soil itself.

a. Comment on use for measuring risk.

- [Mr. Schock] Not really. You have to know all of the site characteristics in order to know the risk associated with the contamination.

b. Comment on use for indicating contaminant mobility.

- TPH does not indicate contaminant mobility.

- Site specific factors must be considered.

5. If a TPH cleanup standard is used, are different cleanup levels appropriate for different petroleum products (i.e. gasoline vs diesel).

- [Mr. Schock] I think different levels are appropriate, but I am not sure technically how you would arrive at those different levels.

6. Please present advantages and disadvantages associated with using a compound specific standard (address risk and mobility considerations).

ADVANTAGES:

- [Mr. Schock] In a general sense, such standards would be more specifically related to the constituents of concern.

- [Mr. Barreth] It directly reflects the known toxic compounds that highest toxicity or detrimental effects.

- [Mr. Mittelsteadt] With a BTEX standard you are dealing with constituents that are well studied and a lot is known about their characteristics.

DISADVANTAGES:

- Focusing on specific contaminants for one petroleum product may not apply to other petroleum products. Therefore, the concern is that some potentially harmful constituents will be overlooked.

7. If a compound specific standard is used, what chemical compounds should be included (identify for different petroleum products)?

- [Mr. Barreth] I am not that knowledgeable on the chemistry of petroleum to answer.

8. Is there any other information/considerations you would recommend we look at in our research?

- "I'll send you a document titled "State of Action Level Guidelines for Gasolines and Petroleum Hydrocarbons" which will explain our RAL's and the criteria we used in evaluating cleanup actions at sites.

- You might talk to some other people in our office such as...
  - Martin Schock (former director) 701-221-5170
  or Gary Barreth

State Regulator Interview: New Mexico

10 May 93

Contact: Mr. Keith Fox
NM Environmental Department, UST Bureau
Health Program Manager
- Three years working with the regulations

2. What cleanup standards and guidelines are currently used by your state for cleanup of PCSs and groundwater?

a. Distinguish between action levels and cleanup levels for each type of petroleum product regulated.

- Action Level: notification is required if contamination is suspected. Action is required if a head-space reading is over 100 ppm. If inspectors find this level they will turn the site in as a release.

- Soil Cleanup Levels: these are strict cleanup levels. Sites must be cleaned up to these levels unless they meet one of the exemptions below.

Gasoline: - Laboratory: 10 ppm benzene
50 ppm total aromatic hydrocarbons

- Field screening: 100 ppm (using an OVA)

Diesel: 100 ppm TPH

- Water Cleanup Levels:

Gasoline: 10 ppb benzene
620 ppb toluene
750 ppb ethyl benzene
620 ppb total xylenes
30 ppb total naphthalenes including all monomethyl naphthalenes
100 ppb MTBE
0.7 ppb benzo(a)pyrene

b. Are your cleanup levels flexible? Why or why not?

- Soil does not have to be remediated if the site meets on of these criteria.

(1) Groundwater below the soil is 10,000 TDS or greater (nonpotable water).

(2) The documented clean interval of clean soil is 50 feet or greater. Need a 50 foot interval between the extent of contamination and groundwater, or greater.

(3) "If it is found by a preponderance of the evidence that methods, technologies, operations, and procedures used by the owner/operator, although not conforming to a regulation will in fact protect health, the public welfare, and the environment to a degree which is equal to or greater than that which is provided by the regulations". This is the mechanism by which owners/operators can incorporate risk based risk analysis as remediation technologies.

- Have not seen many of these exemptions. Mr. Fox has seen only one which the state did not allow, and has heard of a couple of others that have been recommended but not formalized. Mr. Fox believes that this exemption will become more popular.

c. Is risk assessment required for cleanup of PCS? If so, when?

- Not required, but is allowed. See above. Risk assessments have only been proposed once or twice in the state. They are relatively new and fairly unused.

d. If risk assessment is used, does your state consider TPH levels in assessing risk? If so, in what respect? If not, why?

- Would be considered for any of the heavier hydrocarbons, but would not be required for gasoline.

e. How does your state regulate soils contaminated with jet fuel?

- As a heavy fuel. Would require TPH analysis.

f. Does site age make a difference in how PCS is regulated?

- No.

g. Does your state have plans to change the standard? - No

3. Please explain the rationale behind the development of your state's current cleanup standard.

a. What is the technical basis for the standard?

- Benzene is used for gasoline because of the health risks associated with it. Benzene is singled out as an indicator under the assumption that if the standard for benzene is not exceeded then the rest of the aromatic hydrocarbons will not exceed risk levels. Also, the standard for benzene will be the toughest standard to meet

- MTBE is more of an indicator compound standard, rather than a health based standard. Current toxicity information on MTBE shows that there are no health effects associate with MTBE.

- The current standards were established through a thorough review of existing literature, data, and EPA studies done in the late 80's on both health risks and migration of compounds in the soil. Found that 100 ppm by field analysis and 50 ppm by laboratory analysis were good numbers to represent migration.

- Standards were established to be protective of groundwater; "priority was placed on groundwater protection".

- Most of the work done is done through field screening. NM assumes that if TPH is present in the soil, it will be identified through field screening.

b. Was another state's approach (or specific study) used in establishing your standards (i.e. California LUFT manual or Stokeman & Dime's research)?

4. Please present advantages and disadvantages in using a TPH cleanup standard.

Advantage:

- It is a conservative number, the testing method measures a stretch of hydrocarbons (a large number). It somewhat over-estimates the presence of the carcinogenic compounds regulated in groundwater (aliphatics and aromatics)
- TPH is a broad number that applies to all types of compounds. It is good for different mixtures such as waste oil, kerosene, and diesel that do not have target compounds such as BTEX (which is in gasoline). TPH can be used to quantify contamination.

Disadvantages:

- Test methods can be questionable as far as the aromatics are concerned. Preparation can volatilize the compounds. Therefore, only appropriate for the heavier compounds.

a. Comment on use for measuring risk.

- TPH can measure risk to a certain extent. The question is what represents an acceptable risk and what doesn't. Understanding is that high TPH standards have been proposed as acceptable (up to 1,000 ppm).

b. Comment on use for indicating contaminant mobility.

- Can be used to determine mobility potential. There will be certain levels of TPH where it will indicate mobile components or not so mobile components. This is the basis for the state's 50 foot rule.

5. If a TPH cleanup standard is used, are different cleanup levels appropriate for different petroleum products (i.e. gasoline vs diesel).

- Not for gasoline vs diesel, because TPH is not an appropriate test for gasoline.
- For diesel vs kerosene NM does not have a different standard. State would be open to consider different numbers, such as if kerosene was shown at a site to have a low number of aromatics.

- **[Do you feel one standard for TPH would be appropriate for all different petroleum products?]** Yes, at least as an initial cut for cleanup vs non-cleanup.

6. Please present advantages and disadvantages associated with using a compound specific standard (address risk and mobility considerations).

Advantage:

- Standard is helpful when you have a known quantity and health hazard associated with a specific compound. You can use a lot more of the toxicological data for the compound to evaluate risk.
- Can do a risk analysis based on a certain number and get a calculated risk
- Easy to enforce

Disadvantages:

- BTEX standard for gasoline definitely increases costs. It is justified (such as in Michigan where there is a concern for groundwater that must be controlled). On the other hand, you really have to have a mechanism to allow a risk analysis and monitoring only as a remediation option where there is no receptor.

7. If a compound specific standard is used, what chemical compounds should be included (identify for different petroleum products)?

- BTEX for gasoline

- Considered naphthalene for diesel. Currently TPH has been acceptable for the heavier hydrocarbons. NM has not seen the need for trying to enforce other specific standards.

State Regulator Interview: New York

Date: 12 May 93

Contact: Mr. Frank Peduto
N.Y. State Department of Environmental Conservation
Division of Spill Prevention, Response and Remediation
Section Chief, Technology Evaluation Section
(Investigates Remediation Technologies in the Cleanup of Petroleum Contaminated Media)

2. What cleanup standards and guidelines are currently used by your state for cleanup of PCSs and groundwater?

- Standards: are compound specific. Soils magazine left off all of the exponents in their report (i.e. recommended cleanup level for benzene should be 24 ppm).

- TPH analysis is not used for regulatory compliance, but is encouraged for use as a screening tool.

- Notification: any spill of petroleum must be reported, no minimum amount. Reason is because tanks leak in gallons/hour or day. No way of determine how long this has been taking place. If tank test shows in excess of 0.05 gallons per hour it is considered a leaking tank or a spill. Quantity of a spill or leak is not indicative of serious situation.

- If there is no evidence of contamination upon removal of a spill, no action is required. Sampling is required only if contamination exists. Sampling includes samples taken from the side-walls and bottom of the excavation.

- Screening: NY allows any technical tools from visual observation to wet lab analysis, depending on the extent of contamination. TPH is allowed for screening.

- Investigation: purpose is to characterize the extent of contamination. NY does not require soil gas, but may recommend it. Purpose of investigation is to define the plume and confirm with monitoring wells. No definitive requirements. Site specific. State does not define specific requirements because different sites have different requirements for characterization.

- Responsible parties must present a remediation plan which must be reviewed and approved. Plan must identify a monitoring plan, remediation technique, and other specifics.

- Parties performing cleanup commonly used E418.1 and 8015 MOD. These methods are not specifically recommended by NY.

a. Distinguish between action levels and cleanup levels for each type of petroleum product regulated.

- Action Levels: NY state has no action levels. State uses cleanup levels.

- Cleanup Levels: the levels required by the state are exclusive for excavated soils. NY is developing one now for in-situ soils. Right now, NY applies what they have for excavated soils as a goal for in-situ. The levels for excavated soils are strict and must be met.

b. Are your cleanup levels flexible? Why or why not?

- Ex-situ soil standards are used as a goal for in-situ soil. The environmental sensitivity of the area is looked at. Remediation for in-situ soil is site specific. State is beginning to work on regulations for in-situ soil. These regulations will address such issues as the depth to groundwater and distance to down-gradient wells, and whether the site is above a primary aquifer.

c. Is risk assessment required for cleanup of PCS? If so, when?

- NY is just beginning to look at risk assessments for sites contaminated with petroleum. Risk assessments are not encouraged from the standpoint that NY expects responsible parties to clean up the site as much as possible. Mr Peduto believes risk assessments should follow only if the technology to clean the site is not available or the cost/benefits to clean up are not reasonable.

- Another approach (encouraged by private industry), however, is to conduct the risk assessment first to establish a target cleanup level. A site is then cleaned to that level. Mr Peduto questions that if you can do better, why should you stop at the risk based level? Risk assessment values are less stringent in almost all cases.

- NY has a specific law that cleanup must be to pre-spill conditions. If NY really wanted to enforce this law, it could. This, however, is unreasonable, especially in the case of groundwater contamination.

- Problem with risk assessments is the current reliability of the methods used to conduct an assessment. For instance, for models used reliability concerns include: how good is the model, how much variability exists between different models, and what the model considers. There is currently little proof that models predict what will actually take place.

- NY is proceeding cautiously. Believes that risk assessments are going to happen and that they make sense.

- Something similar to a risk assessment is currently used by NY. For instance, NY allows monitoring if cleanup at a site has proceeded to a certain point, the technology to clean up further is limited, and there are no significant impacts from the site. Thus, the levels established under this approach are remediation based cleanup levels. NY has the authority to allow a responsible party to halt remedial efforts if warranted.

d. If risk assessment is used, does your state consider TPH levels in assessing risk? If so, in what respect?

- No

e. How does your state regulate soils contaminated with jet fuel?

- Same as fuel oil

f. Does site age make a difference in how PCS is regulated?

- No

g. Does your state have plans to change the standards?

- Standards are being reviewed. Soil cleanup levels are being reviewed.

3. Please explain the rationale behind the development of your state's current cleanup standards.

a. What is the technical basis for the standards?

(1) Protection of groundwater. Groundwater standards exist for contaminates. Soil standards were established based on the ability of the contaminates to leach to groundwater. TCLP extraction method is used to indicate the leachability. The standards are groundwater values but are also a standard for leachate from contaminated soil (i.e. the extract from soil used in the TCLP extraction process is analyzed for comparison against the standards). A basic assumption was used that all soil is at the soil/water interface. The standard, therefore is conservative.

- Method 8021 (8020) is used to analyze the extract from the TCLP.

- TCLP test involves mixing the soil with a light acid solution, and spinning the mixture for eighteen hours. For volatiles, the mixture is put into a zero headspace extractor. The liquid extract is what is analyzed by method 8021/8020.

- NY is concerned about whether the contaminate leaches. If it doesn't leach, then it is fine for it to be bound up in the soil. If bound in the soil it satisfies the protection of groundwater criteria.

- In NY, all groundwater is considered potable. Standards were to be protective of potable groundwater.

(2) Protection of human health.

- Health based standards for soil are a straight concentration of the substance in the soil (not an extraction like the standards for groundwater).

- standards are EPA numbers that are (basically) based upon ingestion. Strict standards exist for the fuel oils. There are carcinogens in the fuel oils (like the PAHs) that if they are present and are above the standard, they are difficult to remove. These do not appear in all instances (of fuel oil).

- Standards are strict, and some are set at levels below the detection limits. NY's position is that in the cases of standards below detection limits, a site can satisfy the standard if contaminate levels are below detection limits.

- Standards were established in conjunction with NY Health Department, and human health evaluation of the chemicals.

4. Please present advantages and disadvantages in using a TPH cleanup standard:

- Advantage: expedient. "People want to use TPH because it's cheap and because it's quick".

- Disadvantage: measurement is inaccurate. There is no scientific basis in the number. Mr. Peduto believes the number came out of NJ. This state was the first to establish any kind of number. Many others jumped on the bandwagon. NJ now, however, does not even use the 100 ppm standard. The standard is not scientifically based.

- Mr Peduto has seen sample results where the total BTEX has been higher than the levels of TPH measured. This was in several samples.

6. Please present advantages and disadvantages associated with using a compound specific standard.

- Advantage: much more protective of human health. Better handle on what is going on in both the groundwater and the soil.

- Disadvantages: cost and time for lab analysis. Cost is the biggest disadvantage, however.

7. If a compound specific standard is used, what chemical compounds should be included (identify for different petroleum products)?

- See list in Soils Magazine

State Regulator Interview: Pennsylvania

Date: 21 May 93

Contact: Mr. Doug Cordelli
Storage Tank Program
PA Department of Environmental Resources
Hydrogeologist
- Assisted in establishing regulations, assisted in Department review and position on State Statute for UST program

2. What cleanup standards and guidelines are currently used by your state for cleanup of PCSs and groundwater?

a. Distinguish between action levels and cleanup levels for each type of petroleum product regulated.

Cleanup Levels for Gasoline:

Level A: this is the cleanup level. The department accepts this level as "clean". Soil meeting this level is classified as "clean fill". The department has stated in their policy that they would consider sites meeting this level as a clean site. The levels stated in Soils magazine are the "A" levels.

Level B: values are one order of magnitude higher than the "A" values. If soil levels are greater than the "A" levels, but less than the "B" levels, a site is not considered a clean site. However, the state will allow a responsible party to stop cleanup or not initiate cleanup if certain management practices are met. These practices include keeping the volume of soil from groundwater or surface water, or direct contact with humans. Buffer zones must be established. One such buffer zone would be four feet of clean soil (level "A" or below) must exist between the level "B" zone and the seasonal high water level for the site. There are others for surface water, sink holes, wetlands, outcrops, etc.

Level C: policy is somewhat ambiguous. Levels are: 0.4 ppm benzene, 90 ppm toluene, 90 ppm ethyl benzene, 100 ppm total xylenes, no value for TPH. If a site is in-between the "B" and "C" values, some sort of justification must be submitted for why the site cannot be cleaned to level "B" and how the environment and public health will be protected.

Over Level C: unacceptable. Soil must be removed or remediated to level "C" at a minimum.

- Waste Oil and Blended Heating Oils: regulated differently than gasoline. There are no established cleanup values. Cleanup is handled on a case by case basis. Regulations require that responsible parties must clean up everything. The driving force behind all cleanup is the protection of groundwater and the department has a policy of non-degradation. For gasoline the non-degradation policy was used to establish the cleanup values which allow people to not clean up everything.

b. Are your cleanup levels flexible? Why or why not?

- The levels are flexible on a site specific basis. If site specific values are used, and a risk assessment is conducted, the department may approve different cleanup values on an individual site basis.

- The level "B" 100 ppm TPH cleanup level is a nonflexible level unless a party submits a risk assessment that shows that the levels at the site will not cause degradation of groundwater.

c. Is risk assessment required for cleanup of PCS? If so, when?

- A party can do a risk assessment to come up with site specific values, different than the values the department has established [which will be considered by the department].

- Risk assessments are allowed. In the past the department did not allow risk assessments because in the majority of the cases risk assessments were used improperly. People used them as justification to not do anything or to only reach a value currently met as opposed to using the risk assessment to clean up to the lowest levels that can be met.

d. If risk assessment is used, does your state consider TPH levels in assessing risk? If so, in what respect? If not, why?

- For heavy fuels, TPH levels are looked at. In addition, for waste oils or blended fuels the state looks at metals analysis, PCB's, either TOX or PAH's. A responsible party that has this type of release would be responsible for conducting a full priority pollutants scan. State has had problems with people selling a "blended" heating oil that supposedly meet specifications but they had blended in hazardous waste.

-- No target levels have been set by the department for PAHs. Site specific levels can be established for a site using risk assessment.

- **[If levels of metals, PAHs, etc. were low, and met standards, if levels of TPH were high would the TPH levels drive cleanup?]** Yes, TPH would drive cleanup. **[Why?]** Because PA has not established cleanup values for any other substance other than BTEX and TPH.

- **[Would TPH levels drive cleanup of jet fuel if BTEX levels met standards and TPH was above 100 ppm?]** Yes, if BTEX didn't exist, TPH values would be used as a surrogate to represent all other hydrocarbons in the petroleum because there is no established cleanup values for any other compounds. The department would be open to reviewing a risk assessment and negotiating a cleanup value for other hydrocarbons. If a risk assessment is not performed to establish other hydrocarbon cleanup values, however, the TPH level would drive cleanup.

- **[Do you know of any instances where a risk assessment has been performed in PA and the state approved of leaving values above 100 ppm?]** Since the policy has been established (Oct 91), the state has not allowed anyone to leave soil with concentrations of TPH much greater than 100 ppm TPH because not many have done the risk assessments. They just do not want to put the money into it. The state says 100 ppm and people have been removing or remediating to this level.

e. How does your state regulate soils contaminated with jet fuel?

- the same as gasoline.

f. Does site age make a difference in how PCS is regulated?

- No!

g. Does your state have plans to change the standards? (Describe)

3. Please explain the rationale behind the development of your state's current cleanup standards?

a. What is the technical basis for the standards?

- Cleanup values were established by a department risk assessment. The values are generic values to be applied to any petroleum release that is a virgin fuel, these apply to any release.

- In the risk assessment conducted by the state, the state studied concentrations of BTEX that could be left in place. They did not study TPH levels because "there is no toxicological data that can be applied to TPH levels, so you cannot do a risk assessment". "TPH is a host of chemicals that are going to have different physical properties". This is why there is no "C" value for TPH.

- Model used is a Department model which utilized data from Pignatello (1990), desorption kinetics equations from Brusseau (1990/1991), and mass balance equations from Frenstra (1991).

- The "A" values are based on the detection limits of method 8020. If soil is contaminated at level "A" values, according to the fate and transport models used, the soil would not contaminate water to the point that it would be detectible. Thus the states groundwater protection strategy of non-degradation would be met. The standards are based on protection of groundwater.

- Soil at level "B" would cause a detectable degradation of groundwater if the soil was in direct contact with water. With the four foot buffer, however, the soil would not cause a detectable degradation of groundwater.

- TPH values were established strictly on the basis of the method detection limits.

- The level "C" values are based on protecting water (to the MCL) that is in direct contact with soil contaminated to level "C". Theoretically, soil that is contaminated to level "C" will not leach contaminates into the water and create levels above the MCL. There are no values for TPH because there is not an MCL for TPH.

b. Was another state's approach (or specific study) used in establishing your standards (i.e. California LUFT manual or Stokeman & Dime's research)?

- No. The California LUFT manual and Stokeman & Dime's research were used as resources however.

4. Please present advantages and disadvantages in using a TPH cleanup standard.

Advantages: cost and ease of use. Can be used as a surrogate to measure a lot of parameters.

- **[Comment on use for measuring risk.]** TPH cannot be used to measure risk.

5. If a TPH cleanup standard is used, are different cleanup levels appropriate for different petroleum products (i.e. gasoline vs diesel).

- No, levels should be the same.

6. Please present advantages and disadvantages associated with using a compound specific standard (address risk and mobility considerations).

- Mr. Cordelli's opinion is that a compound specific standard should be used for cleanup because then a risk assessment could be performed. A means for negotiating cleanup would then exist because toxicological data on specific compounds could be compared to measured levels; these levels would then be a starting point for negotiating cleanup.

- **[Do you think there would be any disadvantages as far as cost if a compound specific standard was used?]** Mr. Cordelli thinks so, because of the analytical requirements. Significantly more expensive analysis is required as opposed to a TPH analysis, which is inexpensive compared to everything else. With compound specific cleanups, cleanup values should be established for all parameters in the petroleum product for which toxicological data exists. So, may be looking at a dozen or two dozen parameters. To analyze the soil may have to run three or four different analysis to get all the parameters. Analysis costs, therefore, will be significantly more. There is, however, a target value that when you get to the value you're done, which may reduce cleanup costs. With TPH, it's cheaper and quicker and gives a lot of people "a warm and fuzzy feeling" that they know what's going on.

State Regulator Interview: Rhode Island

Date: 21 May

Contact: Mr. Michael Mulhare
Supervising Sanitary Engineer
RI Dept of Env Mgmt
(Site Remediation Section)

2. What cleanup standards and guidelines are currently used by your state for cleanup of PCSs and groundwater?

a. Distinguish between action levels and cleanup levels for each type of petroleum product regulated.

- the numbers provided in the Dec '92 Soils magazine article are probably related to UST situations (removal)

- our cleanup "goals" are kind of a sliding scale

- the way we approach petroleum contamination (in the Site Remediation Section) is a site specific approach. We look at "what the contaminants of concern are", "what the land usage is", "what the principal receptors in the area are". From this information we try to determine what the appropriate cleanup should be.

- we have set cleanup goals for unrestricted land usage at 50 ppm TPH (site wide average)

- any individual sample must be below 100 ppm TPH but the site-wide average must be less than or equal to 50 ppm TPH

- this 50 ppm TPH is for unrestricted land use, you can build houses on it as an example

- this 50 ppm site-wide and 100 ppm individual sample cleanup goal does two things:

(1) calls for a very low number so if there is any other residual problems they are probably of little concern considering the low number of TPH
(2) for "unrestricted land" use we consider aesthetics in addition to the risk from the contamination left behind--"a number less than 100 [ppm TPH] with a fuel oil essentially reduces any odor concerns that you might have

b. Are your cleanup levels flexible? Why or why not?

- yes, but it depends on the site specific factors such as land usage

c. Is risk assessment required for cleanup of PCS? If so, when?

- we do not necessarily require an RA, but often times people will provide one in an effort to usually look for a higher [cleanup] number

- usually the risk based assessments do not address the aesthetics and we feel they are a factor when land usage comes into play

d. If risk assessment is used, does your state consider TPH levels in assessing risk? If so, in what respect? If not, why?

- we use TPH as a cleanup criteria so therefore if someone is doing an RA to justify an alternative cleanup number then they would use TPH in their analysis

- the amount of TPH in the soil does not necessarily tell you anything about the risk of that soil to human health, you must look at the individual parameters

e. How does your state regulate soils contaminated with jet fuel?

- don't recall a strict approach, but what they would do first is identify the "bad actors" of the mixture, they would then tailor their assessment on them

f. Does site age make a difference in how PCS is regulated?

- it really doesn't change our approach, we check for everything in the initial site assessment

g. Does your state have plans to change the standards? (Describe)

- not aware of any

- we believe that going to hard numbers does not allow enough flexibility

3. Please explain the rationale behind the development of your state's current cleanup standards?

- the 50 ppm TPH "site average" was developed in-house

- we looked at what other states were doing at the time and also wanted to put a "level of comfort" in for the Department from future liabilities

-- when looking at other states and what they were doing, we found that the TPH numbers being used (late 80's) were anywhere from 100 to 500 ppm TPH, some were even zero

- also saw some non-detects and some numbers upwards to 1000 ppm

- believes that the state info was obtained from a national survey (probably Kostecki's)

- we have found that the 50 ppm TPH site-wide is very attainable particularly if you allow individual samples to spike up to 100 ppm TPH
    -- 50 ppm removes any odor problems and essentially gives you a relatively clean site
- we also look at VOC's
    -- BTEX compounds are targeted for gasoline
    -- for fuel oils we may look at naphthalene or something like that

a. What is the technical basis for the standards?

- see above

b. Was another state's approach (or specific study) used in establishing your standards (i.e. California LUFT manual or Stokeman & Dime's research)?

- not in particular as far as I know

4. Please present advantages and disadvantages in using a TPH cleanup standard.

- "TPH is just an indicator of what your problem might or might not be"

- recommends measuring for specific compounds using Gas Chromatic test which allows you to tailor the test for the specific compounds??

a. Comment on use of TPH for measuring risk.

- the amount of TPH in the soil does not necessarily tell you anything about the risk of that soil to human health, you must look at the individual parameters

- TPH gives you a way of evaluating what level contamination you have but you have to look at individual compounds in order to adequately address risk

- most risk based data is compound specific

b. Comment on use for indicating contaminant mobility.

- he has never used TPH as an indicator for contaminant mobility

- if they are concerned about contaminant mobility they put in monitoring wells to keep an eye on the GW

5. If a TPH cleanup standard is used, are different cleanup levels appropriate for different petroleum products (i.e. gasoline vs diesel).

- he hasn't used it in that regard, the additional tests we require (BTEX for gasoline as an example) are different for the type of contamination

6. Please present advantages and disadvantages associated with using a compound specific standard (address risk and mobility considerations).

- he feels that if you target the right compound, naphthalene as a PAH for example, then you have an indication of what other PAH's are in the soil

- BTEX, for example is a good representation of gasoline contamination

7. If a compound specific standard is used, what chemical compounds should be included (identify for different petroleum products)?

- BTEX for gasoline

- PAH's for heavier fuels

8. Is there any other information/considerations you would recommend we look at in our research?

- you must recognize its limitations of TPH

- if it is used properly it can be very helpful, if it is used without considering the compounds you are dealing with it can be misleading

Other information provided:

- TPH using the GC (Gas Chromatic) method is much more accurate than other methods available to measure TPH like method 418.1, for example

- a strict cleanup number may reduce the cost of regulating but he thinks it would increase the cost of cleanup and compliance because to come up with an "acceptable" number it would be conservatively low so that not to allow any cases where it is not appropriate

- look at TPH and different constituents in concert with one another

- because petroleum products are so complex, TPH should be used in concert with more compound specific tests

<u>GC vs EPA 418.1</u>

- the 418 can give you false positives because it can pick up organics in soil

- GC is more exacting for petroleum hydrocarbons. There are problems with the GC tests, however...
    - -- if you do not use the right standard the GC method can give erroneous data also

- "if you take the time to tailor your analytical testing to what you are trying to do, TPH can be very effective"

State Regulator Interview: Texas

7 Jun 93

Contact: Ms. Chris Chandler
Texas Water Commission, UST Program
Geologist - Worked with agencies UST program for 5 1/2 years.

2. What cleanup standards and guidelines are currently used by your state for cleanup of PCSs and groundwater?

a. Distinguish between action levels and cleanup levels for each type of petroleum product regulated.

Current:

- no action levels. Any contamination in soil would prompt action, but would not necessarily mean that cleanup would be required.

- cleanup levels: 100 ppm TPH and 30 ppm BTEX. These are for all types of petroleum hydrocarbons.

Future: standard will be a risk based, site-by-site standard.

b. Are your cleanup levels flexible? Why or why not?

Current: each coordinator has the ability to be flexible at a particular site based on the circumstances at the site. The cleanup levels, are basically recommended cleanup levels. In the past, any TPH in the ground was pretty much required to be cleaned up.

Future: will look solely at the public health risk. There will be sites were there are contaminants in place, that do not present risk, and cleanup will not be required.

c. Is risk assessment required for cleanup of PCS? If so, when?

Current: risk assessment is not required.

Future: risk assessment will not be required, although, in most cases a risk assessment will probably be done.

d. If risk assessment is used, does your state consider TPH levels in assessing risk? If so, in what respect? If not, why?

- no. TPH cannot be used in a risk assessment process because details for specific compounds must be used. Because TPH does not define specific compounds, it cannot be used in a risk program. TPH would not drive cleanup in a risk based program because it cannot be used for evaluating risk.

e. How does your state regulate soils contaminated with jet fuel?

- The same as all other hydrocarbons.

f. **Does site age make a difference in how PCS is regulated?**

- No

g. **Does your state have plans to change the standards? (Describe)**

- Yes, see above.

3. **Please explain the rationale behind the development of your state's current cleanup standards?**

a. **What is the technical basis for the standards?**

<u>Current:</u> was somewhat derived from the LUFT manual. Used the concept but established specific numbers for Texas.

<u>Future:</u> will not have any specific numbers. Methods will be standard risk assessment methods as put forth in the RAGs Superfund documents (and others). Standard calculations for risk assessment will be used under this standard.

4. **Please present advantages and disadvantages in using a TPH cleanup standard.**

a. **Comment on use for measuring risk.**

- TPH cannot be used in a true risk based program because it is not compound specific. Can possibly develop something that correlates TPH to a specific compound by putting some default values into the calculations, but would not be detailed or standard.

- TPH can be useful as a general number, but there are many problems. Standard analytical methods for TPH have problems with the numbers that you get, they may not be accurate.

- TPH cleanup goals have been used for the life of Texas's program, but, it is not always a good measure of the risk associate with the site.

b. **Comment on use for indicating contaminant mobility.**

- Cannot use TPH to indicate mobility because you don't know what the TPH number represents.

- **[Why is it used?]** Because it is a simple and inexpensive analytical method. Some states don't use it, but Texas has because they have not felt that it was necessary to go to a compound specific standard (something more difficult). But with a risk based program, you pretty much have to go to a compound specific standard.

5. If a TPH cleanup standard is used, are different cleanup levels appropriate for different petroleum products (i.e. gasoline vs diesel).

- No.

6. Please present advantages and disadvantages associated with using a compound specific standard (address risk and mobility considerations).

Advantages:

- Can run a risk assessment with specific compounds, as opposed to using a TPH number.
- If using a specific compound, you will know the mobility of that chemical.

Disadvantage:

- Added cost for analysis
- Additional work and time on the part of the consultants and the regulators.

7. If a compound specific standard is used, what chemical compounds should be included (identify for different petroleum products)?

- BTEX and polynuclear aromatic hydrocarbons. Will not have a separate standard for separate hydrocarbons - an old gasoline can look like diesel. State is concerned about what is truly there, rather than what leaked in the first place.

- For used oil releases, state looks at metals

8. Other: basis for future standard

- Low cleanup levels are the most conservative and are the safest, but are also the most expensive. What Texas is doing is cutting the expense to the bare minimum necessary to protect public health and safety. This will mean that contaminants will be left in the ground. The health and safety risks, however, will be taken care of to where the risk is an acceptable risk.

- In the past Texas had strict cleanup levels. Now, the state does not have the money to fund all the cleanups. Texas needs to study which sites are the most important to clean up (the ones with the greatest risk).

- It is really an economics thing. It would be great to clean up all sites to where they are absolutely clean, but there is not enough money in the world to do this. So, we have to go with the next best option.

- Talked to other states and more and more states are looking at going to a risk based program. In reality a risk based program makes a lot of sense. Cannot satisfy everyone, however, in the future once thousands of sites are cleaned up then maybe eventually there may be money to go back and redo some of them.

State Regulator Interview: Virginia

Date of Interview: 11 May 93
& 21 Jun 93

Contact: Mr. Dave Chance
Env Program Mgr
VA Dept of Env Quality
Ph: 804-527-51888

2. What cleanup standards and guidelines are currently used by your state for cleanup of PCSs and groundwater?

- VA does not have any set "cookbook" action levels or cleanup numbers established. VA is site specific in our cleanup methodology.

- VA uses 100 ppm TPH as a "guidance level" (see 2a. for explanation)

- Normally for PCS, our cleanup parameters are TPH and BTEX, but the cleanup levels are "site specific".

- "VA's program for petroleum contaminated soils and GW cleanup "endpoints" is simply that the "endpoints" are based on "site specific" data including site risk and remediation data."

- if a TPH level comes back from a site greater than 100 ppm TPH the Regional Office has the authority to require or do one of the following:
    - -- site check (for a suspected release)
    - -- closeout the site

- a level above 100 ppm TPH is more or less a signal to the Regional Office staff that maybe we need to look a little closer at the specific site

- if a level below 100 ppm TPH is found VA may still require further action if the site is close to a drinking water supply for example

- the 100 ppm TPH is not a hard and fast guidance (i.e. there are other things that may come into play)

- VA may require a "Site Characterization Report" (SCR) if they determine that a release has occurred
    - -- tank owners must sample with analytical methods that are appropriate for the type of contamination
        - --- as an example if a gasoline release has occurred we require testing for BTEX and not TPH

a. Distinguish between action levels and cleanup levels for each type of petroleum product regulated.

- the only guidance number VA uses is a TPH number of 100 ppm for "clean" tank closure. This means that when a tank is removed VA "generally" issues a clean site closeout letter if the following two conditions are present:

(1) there is no visible evidence of contamination
(2) soils samples are still to be taken from the bottom of the pit and
if TPH #'s come back less than 100 ppm.

- VA makes it clear that a clean site closeout letter does not exempt the tank owner from further action if required

-- require approved EPA methods for measuring TPH
-- most commonly see EPA method 418.1 (modified for soils)

b. Are your cleanup levels flexible? Why or why not?

- Yes. We require an SCR for confirmed releases and samples above 100 ppm TPH. From this information the responsible party indicates what they think is an appropriate endpoint for cleanup and what technology they think should be used. We then evaluate the recommendation.

c. Is risk assessment required for cleanup of PCS? If so, when?

- Yes, RA is required in developing "corrective action plans." A Risk Assessment is incorporated into the SCR and the information from the SCR determines whether or not corrective action is warranted.

- If an SCR is required, it includes the following:

(1) what contaminants are involved
(2) the geology and hydrogeology of the site
(3) the degree and extent of the contamination
    --- lateral
    --- vertical
(4) all phases must be addressed in this report
    --- vapor phase
    --- soil phase
    --- dissolved phase
    --- free product phase
(5) once all of the phases are addressed, then they must develop a risk assessment for each phase of the contamination

- the following factors must be addressed in the risk assessment portion of the SCR and "corrective action plan":

-- what are the exposure pathways?
-- what are the potential receptors? such as...
    --- human
    --- biological
    --- resource (predominately GW)

- based on what the risk is, the tank owner must include in the SRC what they think is an appropriate endpoint for cleanup and what technology they think should be used

- VA "tries" to keep a balance between what is technology and economically feasible for cleanup

d. If risk assessment is used, does your state consider TPH levels in assessing risk? If so, in what respect? If not, why?

- No. There are no toxicity numbers available for TPH as far as I know.

e. How does your state regulate soils contaminated with jet fuel?

- same as we do diesel fuel.
- "guidance level" applies to all petroleum contaminants, but when further site characterization is required VA has set methods for specific contaminants
- VA treats fuel oils the same as diesel
- VA treats gasoline different because of the additives (esp. BTEX)

f. Does site age make a difference in how PCS is regulated?

- No.

g. Does your state have plans to change the standards? (Describe)

- would have to change their state regulations in order to change the way that they do business

- expects them to stay the same

[Do you treat soils in the saturated zone differently than soils in the unsaturated zone?]

- VA doesn't generally look at soils in the SAT zone
    -- it becomes a GW cleanup issue

3. Please explain the rationale behind the development of your state's current cleanup standards?

- VA's "way" is designed "to match the cleanup to the degree of risk and the scope of the problem"

- VA does not believe it is technologically possible or economically feasible to cleanup to background or drinking water type numbers

- VA has a fund designed to help responsible parties in their remedial action costs and because of this...
-- a goal of the VA Dept of Env Qual. is to strongly consider economic factors in their regulatory actions

a. What is the technical basis for the standards?

- overall, VA's strategy is "site specific based on risk"

- VA's goal is to have the most cost effective, site specific cleanup they think is protective of a resource (GW) or an identified receptor

- soil cleanup requirements are designed to protect GW

b. Was another state's approach (or specific study) used in establishing your standards (i.e. California LUFT manual or Stokeman & Dime's research)?

- the 100 ppm TPH guidance level is loosely based on research done in N.J. (Stokeman and Dime)
-- therefore, below 100 ppm TPH you would not expect anything harmful to come out of soils contaminated below 100 ppm TPH and therefore you would not expect any risk

- they recommend the CA LUFT method for TPH analysis

4. Please present advantages and disadvantages in using a TPH cleanup standard.

a. Comment on the use of TPH for measuring risk.

b. Comment on use for indicating contaminant mobility.

ADVANTAGES:
- TPH can be a representative number for contamination such diesel fuel, jet fuel, home heating fuel because it is such a minor component in these fuels.

DISADVANTAGES:

- The main disadvantage is that there is no toxicity data available expressed as TPH.

- TPH really does not really tell you about the migration potential of a contaminant.

  -- You can, however, estimate the potential for GW contamination for such fuels as diesel when you know the site conditions (type of soil, GW proximity, etc.) and the TPH levels. In other words, if you have high levels of TPH at a diesel fuel site and the GW table is high you will probably contaminate the GW.

- TPH is not appropriate for gasoline. For example: if you had a gasoline spill, a TPH number is not going to tell you enough.

  -- applying a TPH standard to a gasoline leak does not make sense because of the BTEX in gasoline

    --- both BTEX and TPH must be looked at

5. If a TPH cleanup standard is used, are different cleanup levels appropriate for different petroleum products (i.e. gasoline vs diesel).

- No. You must look at particular constituents when dealing with different petroleum products.

6. Please present advantages and disadvantages associated with using a compound specific standard (address risk and mobility considerations).

ADVANTAGES:

- there is no human health risk from TPH, therefore a compound specific is obviously a better measure because of available toxicity data. For example, there are MCL's and health based numbers on the BTEX components.

DISADVANTAGES:

- there are a lot of constituents in fuels that we do not know enough information about

- you may test for specific constituents and find none, but at that same site, a TPH measurement may be high.

  -- if this is the case it isn't acceptable to leave a mess in the ground with a potential to leach to the GW even if the BTEX level is negligible because...

    --- may have taste and odor problems

  -- as a result, if you cannot drink the water because of aesthetic reasons it is no more useful than water contaminated with BTEX.

7. If a compound specific standard is used, what chemical compounds should be included (identify for different petroleum products)?

- BTEX is an accepted surrogate for gasoline contamination because of the known hazard associated with these constituents and their mobility potential

- In VA, we generally look at (for) naphthalene for the middle distillates

- for heavier fuels we do look at any particular compounds. We have the preparer of the RA suggest what would be the best indicator parameter.

[Please comment on the appropriateness of a single cleanup standard for all petroleum contaminated soils.]

- there are too many site specific factors to make a universal standard appropriate

- you would have to quantify your numbers... maybe set-up numbers with specific conditions

- he knows of states that have used and since abandoned "cookbook" numbers for the following reasons:
    - -- difficulty in reaching arbitrary numbers in all types of different geological settings
    - -- great expense involved in sometimes reaching those numbers when there is no clear cost benefit associated with getting down to that particular "cookbook" number
        - --- [would not say which particular states]

8. Is there any other information/considerations you would recommend we look at in our research?

- talk to the states that have tried to establish "cookbook" numbers and have since changed from that line of thinking

Additional comments provided:

- the potential for higher weight hydrocarbons (other than BTEX) to migrate to GW is dependent on....
    - -- type of soil
    - -- concentration in the soil
    - -- proximity to the GW
    - -- transitivity of the aquifer

State Regulator Interview: Washington

Date of Interview: 14 June 1993

Contact: Ms. Lynn Coleman
Environmental Engineer
WA State Dept. of Ecology
P.O. Box 47600
Olympia, WA 98504-7600

1. Please state your name, title, and agency. Please describe your expertise and experience in regulating Petroleum Contaminated Soils (PCSs).

EXPERIENCE:

- involved with field work/overseeing petroleum UST removals

- wrote portion of existing guidance document used by state of WA for remediation of releases from UST's

- wrote analytical protocols used by state of WA for PCS

2. What cleanup standards and guidelines are currently used by your state for cleanup of PCSs and groundwater?

FOR SOIL:

- gasoline contamination:	100 ppm TPH (definition of "clean close") .5 ppm Benzene 20 ppm Ethyl-Benzene 40 ppm Toluene 20 ppm Xylene 250 ppm Total Lead

- diesel (and heavier fractions of petroleum): 200 ppm TPH

- We recognize that in a lot of cases the numbers we have established are pretty low and in some cases either technology is not available to achieve these numbers or that achieving these numbers would be cost prohibitive.

-- In these cases we usually require treatment of "hot spots" (the highly contaminated materials or the materials that are very close to a sensitive receptor) and then we require the responsible party to prevent exposure to other materials that is still above cleanup levels by institutional controls.

- If levels are above our established levels we require the responsible parties to prevent exposure to all of the materials above the established level (100 ppm for gasoline for example).

- When we say "cleanup level", that does not mean that all of the material has to come out of the ground or GW

a. Distinguish between action levels and cleanup levels for each type of petroleum product regulated.

- cleanup levels and standards used in WA are levels we have established to be protective of human health and the environment
  - -- they are criterion for a "clean close" whereby a responsible party can walk away from a site with no further liability from a site remediation standpoint

b. Are your cleanup levels flexible? Why or why not?

- We are [illegible]ery flexible on our cleanup levels (our established numbers). We are flexible on how a responsible party <u>prevents</u> exposure to the materials (soil) that exceed those numbers and what the responsible parties do to the soils that exceed the set levels.

- We consider the proximity of the contamination to potential receptors or GW in determining what action is required to remove or remediate contamination but our established numbers are not flexible.

- A key consideration is GW contamination and potential for leachabilty into the GW. Our GW is often very close to the surface.

c. Is risk assessment required for cleanup of PCS? If so, when?

- No. RA is never absolutely required for PCS. It can be done if our Agency thinks it is appropriate.

d. If risk assessment is used, does your state consider TPH levels in assessing risk? If so, in what respect? If not, why?

- We do not have a good methodology for a "canned" RA using TPH, but we allow its use.

e. How does your state regulate soils contaminated with jet fuel?

- We break contaminants out by Carbon chains and require specific analytical protocols based on this. for example:
  - -- gasoline contamination is defined as C_6 to C_{12}
  - -- diesel contamination is defined as C_{13} to C_{24}

- Wherever jet fuel fits in to these Carbon ranges determines the cleanup level

f. Does site age make a difference in how PCS is regulated?

- We require sampling regardless of the age of the site. If the analysis of the petroleum indicates that the site is weathered we may require a different action than what we would if the analysis indicated relatively new contamination.

g. Does your state have plans to change the standards? (Describe)

- We are currently evaluating them relative to how you do RA.

3. Please explain the rationale behind the development of your state's current cleanup standards?

- WA's cleanup numbers are currently based on our "best professional judgement" about potential contamination of GW.

a. What is the technical basis for the standards?

- We do not have any scientific data to back our numbers up.

b. Was another state's approach (or specific study) used in establishing your standards (i.e. California LUFT manual or Stokeman & Dime's research)?

- About 5 yrs ago we contacted about 6 other states when we developed our numbers. We found our numbers were in "the ball park". The range of TPH numbers being used were typically between 50 ppm and 1000 ppm.

4. Please present advantages and disadvantages in using a TPH cleanup standard.

ADVANTAGES:

- You are quantifying a larger percentage of the contamination with TPH than you are with looking at particular constituents (such as BTEX for gasoline). We use specific analytical protocols to quantify the area under a GC curve based on the number of carbons. We use this to determine where most of the range of contamination is.

DISADVANTAGES:

- "We don't have any data about the toxicity of TPH." Because of this lack of information on the toxicity of TPH, we use TPH in more of a qualitative or semi-quantitative way for actual RA.

a. Comment on use for measuring risk.

- Only in a qualitative way. For example, we typically consider a measurement of 1000 ppm TPH of the gasoline fractions more toxic than a measurement of 1000 ppm TPH of the diesel fractions.

b. Comment on use for indicating contaminant mobility.

- We feel that our required analytical protocols for TPH provide an indication of mobility. This reason for this is that we ask for specific fractions in our TPH analysis. If we find lighter range fractions from the analytical protocols we consider them more mobile if heavier fractions were measured.

5. If a TPH cleanup standard is used, are different cleanup levels appropriate for different petroleum products (i.e. gasoline vs diesel).

- Again, we define our fractions based on the number of carbons in the contaminant. Therefore, we fit the petroleum contaminant into one of the following ranges: gasoline, diesel, or heavier fractions. We do not have specific standards for specific types of fuels. I believe that the 100 to 200 ppm TPH is low enough to be effective for all types of fuels.

6. Please present advantages and disadvantages associated with using a compound specific standard (address risk and mobility considerations).

ADVANTAGES:

- You do have toxicity data on some of the individual constituents such as the BTEX components, some of the PAH's, and some of the more volatile fractions.

DISADVANTAGES:

- The data that we do have represents a very small fraction of the entire range of petroleum. What are you are doing then is saying that "these few constituents are representative of the entire petroleum product. And based on that I think you can grossly over- or grossly underestimate the toxicity of the product."

- I think that not enough is known about of all the constituents to ignore but just a few.

- I believe that if you wanted to take an extraordinarily conservative approach you can say that all of gasoline or that all of diesel is as toxic as benzene. This, I believe, would grossly overestimate the toxicity of the petroleum product.

7. If a compound specific standard is used, what chemical compounds should be included (identify for different petroleum products)?

- For gasoline, we look at TPH, BTEX, and lead if necessary.

- For diesel fractions, we do not ask for BTEX because there is typically not much BTEX in diesel or in the heavier fuels.

- For the heavier fuels we may take a look at some of the metals in addition to the TPH levels.

8. Is there any other information/considerations you would recommend we look at in our research?

- You may want to talk to the following two people on our staff:

(1) Charles Sanwan Hydrogeologist Ph: (206)438-3073
- worked on our protection of GW soil matrix

(2) Craig McCormick Toxicologist Ph: (206)438-3013
- he is working on answering the question, "How do you do RA on complex petroleum mixtures."

State Regulator Interview: Wisconsin

Date of Interview: 10 May 93
& 21 Jun 93

Contact: Ms. Laurie Egre
Tank Response Unit Leader
WI Dept. of Natural Resources LUST Program
Madison, WI

1. Please state your name, title, and agency. Please describe your expertise and experience in regulating Petroleum Contaminated Soils (PCSs).

EXPERIENCE: - 3 1/2 yrs experience at current position

EDUCATION: - B.S. in Soils Science

2. What cleanup standards and guidelines are currently used by your state for cleanup of PCSs and groundwater?

a. Distinguish between action levels and cleanup levels for each type of petroleum product regulated.

FOR SOILS (CURRENT):

- WI currently has an "action level" of 10 ppm TPH for PCS. This 10 ppm "action level" applies to:
  - gasoline
  - diesel fuel
  - crude oil &
  - No. 6 fuel oil
  - and others

- WI has used 10 ppm TPH as an action level for about 4-5 yrs

- This "action level" means that if soil sample levels (from tank excavation sites) exceed 10 ppm TPH further action is required

- further action involves a more thorough investigation of the contamination

  -- In the investigation phase more than just TPH is looked at. We also require screening for volatile compounds, PAHs, etc.

- contaminated soils below the GW table are considered a GW problem in most cases

FOR GW:

- TPH is still looked at as an indicator but WI only has specific groundwater standards for volatile compounds such as benzene.

- Our GW standards are based on public health concerns and environmental protection.
- Benzene is of primary concern because it is a known carcinogen and "is very mobile in the environment"

- WI's GW standards have two tiers:
  (1) protective action level
  (2) enforcement standard

b. Are your cleanup levels flexible? Why or why not?

- Yes. If contamination is present above our action levels we may allow the responsible party to leave the contamination in the ground in some cases. As an example, if there are no volatiles present or the contamination is impossible to remove (say it is under a building) we may allow the responsible party to leave the contamination in the ground. We may also require a notice on the deed regarding residual contamination.

c. Is risk assessment required for cleanup of PCS? If so, when?

- We discourage RA because it is time consuming. Because our statutes require cleanup in the event of a release the responsible party must demonstrate that it would be to infeasible to cleanup the contamination.

- Performing a risk assessment at every site is unrealistic for the following reasons:
  (1) excess financial burden
  (2) doubts as to the confidence of the results of an RA (with standards you always know what your target is)
  (3) WI does not have the manpower to do this

- WI's approach to contaminated soils and GW is driven by standards as opposed to individual risk assessment (required by statute)

- We are going in this direction because that is what the public and the regulated community is asking for. "They are asking for a known standard so that when they begin a cleanup they know where their endpoint is." One of the reasons we (WI) agreed to this is because we do not have the staff to evaluate risk assessments.

d. If risk assessment is used, does your state consider TPH levels in assessing risk? If so, in what respect? If not, why?

- N/A

e. How does your state regulate soils contaminated with jet fuel?

- WI groups jet fuel with diesel fuel and the lighter fuel oils

- WI treats jet fuel the same as other petroleum products (i.e. contamination above 10 ppm TPH requires investigation and probable cleanup.

f. Does site age make a difference in how PCS is regulated?

- Site age does not make a difference in how WI regulates PCS. It depends on residual levels of contamination in the soil. Site age may, however, impact the remedial action that is undertaken. Regardless of site age, all responsible parties must define the extent of contamination.

g. Does your state have plans to change the standards? (Describe)

FUTURE SOIL CLEANUP LEVELS:

- new state soil cleanup levels are currently under development

- TPH will still be used as a screening measure for contamination

- we have proposed compound specific soil cleanup standards (BTEX compounds and/or other specific compounds)

- Our new soil standards (coming out when???) are based on existing groundwater standards. WI uses MCLs if available.
  -- Our proposed standards were calculated via a sort of a back-calculation process using a SESOIL modeling process

3. Please explain the rationale behind the development of your state's current cleanup standards?

- at the time WI adopted 10 ppm TPH as an "action level" it was the limit of detection. In other words, anything that could be detected required further investigation

- WI has a hazardous substance "Spill Statute" which has simple language stating that spillers are obligated to "restore the environment" in the event of a release

  -- this statute has been widely interpreted to mean that all contamination will be cleaned up regardless of risk (hence the 10 ppm action level--lab detection limit)

  -- We are in the process of establishing numeric cleanup standards for specific compounds, which will clarify the intent of the statute

a. What is the technical basis for the standards?

- 10 ppm TPH was the lab detection limit at the time it was established

b. Was another state's approach (or specific study) used in establishing your standards (i.e. California LUFT manual or Stokeman & Dime's research)?

- no. Lab detection limit for 10 ppm "action level"
- For cleanup standards we contacted many other states before selecting the SESOIL modelling process (many states contacted were using it)

4. Please present advantages and disadvantages in using a TPH cleanup standard.

a. Comment on use for measuring risk.

b. Comment on use for indicating contaminant mobility.

ADVANTAGES:

- I do not see any particular advantages in using TPH as a cleanup standard for PCS.

- From a cost perspective sampling for TPH is relatively cheap and simple.

- TPH is an indicator of contamination and if TPH levels are above our action levels further action is required to close out a site.

DISADVANTAGES:

- TPH does not give you enough information to model contaminant movement/migration to a potential receptor (far to complicated). Therefore, we would not want to base our soil standards on a measurement that tells us nothing about transport. As a result, we feel it is more appropriate to focus on more mobile and more toxic compounds such as BTEX compounds.

- a TPH level alone does not tell you anything about risk. For example, you could have a weathered site where all of the VOC's are gone yet still have a high TPH levels but relatively low risk.

5. If a TPH cleanup standard is used, are different cleanup levels appropriate for different petroleum products (i.e. gasoline vs diesel).

- TPH is just used to indicate contamination. If contamination is present we require the responsible party to look at the BTEX components which have a relatively high potential to contaminate GW.

6. Please present advantages and disadvantages associated with using a compound specific standard (address risk and mobility considerations).

ADVANTAGES:

- Using specific compounds such as BTEX allows you to model contaminant mobility and its potential to contaminate GW

DISADVANTAGES:

- You may not have a real good match between the specific compound being looked at and the total petroleum contamination released.

7. If a compound specific standard is used, what chemical compounds should be included (identify for different petroleum products)?

- the BTEX components should be looked at all sites because they are present in all fuels, are mobile, and are toxic

- PNA's are looked at for some fuel oil contaminated sites

- We also look for MTBE at some gasoline contamination sites

- We may also look at heavy metals from waste oil contamination

8. Is there any other information/considerations you would recommend we look at in our research?

- You may want to contact Mike Barden. He works for the WI Dept. of Natural Resources and is directly involved in developing the new WI standards. His phone number is:

-- 608-264-6007

FURTHER INFO PROVIDED:

- WI believes the analytical methods used to measure contamination are critical, i.e. states must have appropriate requirements in place for measuring/detecting contamination

- WI requires different analytical methods to measure different types of contamination

- WI has in place specific procedures for the investigation of sites

- I'll send you a draft copy of "Procedures for Establishing Env Restoration Standards for Leaking Underground Storage Tank Remediation Actions". It contains further information that may be of use to you.

State Regulator Interview: Wyoming

Date of Interview: 12 May 93

Contact:
Mr. LeRoy Feusner
UST/LUST Program Director
WY Dept of Env. Quality
Water Quality Division
Ph: 307-777-7096/7075

Mr. Shawn Sullivan (Interviewed 17 Jun 93)
LUST Remediation Program
WY Dept of Env. Quality
Water Quality Division

2. What cleanup standards and guidelines are currently used by your state for cleanup of PCSs and groundwater?

FOR GASOLINE (soils):

- "Action Level" of 30 ppm TPH if GW within 50 ft of contaminated soils
- "Action Level" of 100 ppm TPH if GW greater than 50 ft away from contamination

FOR DIESEL, FUEL OIL, & WASTE OIL (soils):

- "Action Level" of 100 ppm regardless of GW proximity

FOR LEADED FUELS (soils):

- "Action Level" of 5 ppm (Heavy Metals such as lead)

- currently the same as listed in the Dec. '92 Soils magazine article [see above], but in the process of adopting rules and regulations which will implement both a TPH and chemical compound specific calculation method (see more under 5b.)
  -- our new methods are geared towards site specific information

- for GW our goal is to achieve cleanup to the MCL values

- for soils, if we do not first meet the TPH criteria in terms of petroleum we will look first at fate and transport coupled with environmental risk

a. Distinguish between action levels and cleanup levels for each type of petroleum product regulated.

- levels below the "action levels" are required for "clean closure"

- if there are measurements above the "action levels" we may require further action (fate and transport calculations coupled with environmental risk-dose)

-- (for petroleum sites): if they can meet the TPH criteria (as listed in the Soils magazine article), we (WY) hypothesize "that it will be well within the criteria of any BTEX concentration" that may pose risk greater than $1x10^{-6}$ under any scenario

- [Mr. Sullivan] if a responsible party fails the TPH test, essentially, then we require a look at additional items. For example, the responsible party would have to determine what specific constituents are present in order to determine the cleanup action. (see DRAFT "Procedures for Establishing Env Restoration Standards for Leaking Underground Storage Tank Remediation Actions" for further info)

b. Are your cleanup levels flexible? Why or why not?

- [Mr. Sullivan stated that] in the sense that TPH is used as a "first cut". We may then require a look at the volatiles.

c. Is risk assessment required for cleanup of PCS? If so, when?

- [Mr. Sullivan] when the levels are above our "action levels" WY does not require RA the way most people think of RA. we concentrate on site specific data which is based on a fate and transport model. (see the guidance document sent by Mr. Feusner)

- when soils samples at tank sites are above the values listed in the Soils magazine we may require...
  -- a fate and transport coupled with env. risk,
    --- from this, the final remediation number will be the lowest of the two evaluation processes
  -- "what's unique about this methodology is that it attempts to consider as much site specific geological criteria as possible to make the cleanup levels as realistic as possible based on those local parameters"
- use $1x10^{-6}$ for cancer potency factors

d. If risk assessment is used, does your state consider TPH levels in assessing risk? If so, in what respect? If not, why?

- in our proposed guidance specific compounds are used in the event RA is required at a site and not TPH
  -- we use specific compounds because toxicity information is available (toxicity info is not available for TPH)

e. How does your state regulate soils contaminated with jet fuel?

- [Mr. Sullivan] I believe jet fuel is treated as fuel oil [100 ppm TPH]

f. Does site age make a difference in how PCS is regulated?

- [Mr. Sullivan] not in particular, our screening requirements are the same regardless of site age. Age of the site, however, will dictate cleanup requirements because at a weathered site the volatile fraction are usually gone.

g. Does your state have plans to change the standards? (Describe)

- currently the same as listed in the Dec. '92 <u>Soils</u> magazine article, but in the process of adopting rules and regulations which will implement both a TPH and chemical compound specific calculation method--not a full blown RA but a methodology (see more under 5b.)

- in terms of UST/LUST, WY will be looking at BTEX plus any hazardous substances that may have been stored in an underground tank

- WY's new soil remediation criteria will be based on the evaluation of the following two aspects:

(1) "potential to contaminate existing GW quality"
(2) "potential adverse public health impacts will be evaluated using an environmental risk assessment process for contaminated soil ingestion and inhalation."

- as a result, "site specific soil remediation standards shall be determined by the department based on whichever value is lower" (Draft copy, pg. 1)

- see Draft for further info

3. Please explain the rationale behind the development of your state's current cleanup standards?

- our soil cleanup policies are designed to protect GW
- proposed standards were selected to protect GW

- GW standards (or goal) is to cleanup to MCL's
- the cleanup of soils is driven by their threat to GW

a. What is the technical basis for the standards?

- [Mr. Sullivan] it is my understanding that the "action level" numbers WY uses are low enough that there should be a pretty good margin of safety

- [Mr. Sullivan] not sure of any research studies verifying our numbers. It is my understanding that the numbers were commonly used numbers (amongst other states) when WY adopted them.

b. Was another state's approach (or specific study) used in establishing your standards (i.e. California LUFT manual or Stokeman & Dime's research)?

- the (new) TPH criteria WY is proposing has been selected based on Stokeman's study in NJ to protect GW to MCL concentrations

4. Please present advantages and disadvantages in using a TPH cleanup standard.

ADVANTAGES: [Mr. Sullivan]

- TPH is easy to do
  - -- cheap
  - -- gives a general idea of what the contamination is
- TPH is a good screening tool
  - -- provides you with a low cost indication of what may be in the soil

DISADVANTAGES: [Mr. Sullivan]

- not necessarily representative of what the contamination is
- you may miss important compounds when looking at TPH such as the volatile organics
- by itself it may be misleading if you do not have enough additional information about the site

a. Comment on use for measuring risk.

- TPH does not tell you anything in terms of risk
- must look at individual compounds to consider risk assessment
- comparing the two would be like comparing apples to oranges

b. Comment on use for indicating contaminant mobility.

- [Mr. Sullivan] we only use our TPH action levels to close the site and not as an indication of contaminant mobility

- in the case with petroleum, you really only need to look at benzene because it is the most mobile. Poly-nuclear aromatics may be just as toxic but there mobility is nil compared to benzene

- he thinks that if you take care of benzene, regardless of your remediation process, you'll take care of everything else in the process

5. If a TPH cleanup standard is used, are different cleanup levels appropriate for different petroleum products (i.e. gasoline vs diesel).

- see breakout in Soils magazine

6. Please present advantages and disadvantages associated with using a compound specific standard (address risk and mobility considerations).

ADVANTAGES: [Mr. Sullivan]

- allows to look at specific constituents which are known to be hazardous
- a compound specific standard could possibly be a better

DISADVANTAGES: [Mr. Sullivan]

- looking at each compound would be more expensive (on the analysis) and require a more detailed effort (more things to look at)

7. If a compound specific standard is used, what chemical compounds should be included (identify for different petroleum products)?

- Compound specific standard not used

8. Is there any other information/considerations you would recommend we look at in our research?

Other additional information provided:

- he doesn't feel that risk assessment is necessary for petroleum contamination because...
  - -- most LUST sites are buried and there are no pathways of exposure except GW

- regardless of the risk presented in GW contamination it is WY policy to clean up all contaminated GW to MCL's

- WY policy is to protect GW as a potential drinking water source

- basically, all aquifer's will be protected to drinking water criteria

- he sent me the proposed new standards/policies of UST/LUST in WY
  - -- titled "Procedures for Establishing Env Restoration Standards for Leaking Underground Storage Tank Remediation Actions"

-- [Mr. Sullivan] there is no indication that out "action level" numbers (i.e the TPH numbers discussed above) will change even though we have new proposed procedures.

Technical Expert Interview

Date of Interview: 17 Jun 93

Contact:
Dr. Bruce Bauman
Senior Environmental Scientist
American Petroleum Institute (API)
Ph: 202-682-8000
Fax: 202-682-8270

1. Please state your name, title, and agency. Please describe your expertise and experience with petroleum contaminated soil (PCS).

EDUCATION:

- PhD in Soil Science

EXPERIENCE:

- involved with the issues of petroleum contaminated soils (PCS) since 1985 (arrived at API in 1985)

- Involved with a number of research projects in this area which include:
  -- evaluation of state regulations for soil contamination and remediation activities

2. Comment on the importance of risk assessment in developing PCS cleanup standards or approaches.

- I am a strong proponent for RA of contaminated soils

- I feel that RA is very important in developing PCS cleanup standards

- The alternatives (to RA) that have been used are what I term as generic cleanup standards. I feel the numbers that have been used by states for TPH and BTEX, for the most part, are not very well based in science. There are some states that made an effort to add some science to their evaluation but when they do so they typically make worst case assumption.

- With hydrocarbons the pitch I make is that the petroleum hydrocarbons are not going to be persistent over time. The level of contamination in soils should decrease over time due to biodegradation, volatilization, and leaching.

- PCS cleanup criteria should be developed on a risk based approach. Must consider site specific data such as GW proximity.

3. What risk assessment criteria are important in establishing a PCS cleanup standard? Which is most important and why?

MOST IMPORTANT:

- the existing quality and use of the GW that might be impacted is probably the most important when dealing with subsurface petroleum contamination. The reasons why are:
  - -- low quality GW should allow for much higher cleanup levels
  - -- if the GW is a drinking water source or potential drinking water source then more stringent cleanup criteria are warranted

OTHER IMPORTANT CRITERIA:

- the volume of soil that is contaminated
- the concentration of the contaminant in the soil
- if there is any uncontaminated soil between the contaminated soil and the GW

[Do you think soil ingestion is a concern?]

- most of my experience is with Gasoline Station contamination where the contaminated soil is covered by pavement
  - -- but in cases where surface soils are exposed, I think that biodegradation should not concentration down very readily for surface soils in a short period of time

4. Should separate standards be established for different petroleum products (i.e. gasolines, middle distillates, diesel, heavy fuels)? Why or why not?

- I consider diesel a middle distillates

- For gasoline and the middle distillates I think that BTEX are a better criteria than total contamination present.

- For the heavier fuels you have a much different situation in terms of the mobility of the contaminants and the kind of constituents present. With the heavier fuels you have a lot more PNA's presents.

- I think that it makes sense to have separate standards for the following categories: gasolines, middle distillates, heavy fuels (as long as they are risk based).

- In terms of GW quality, the BTEX constituents should drive cleanup standards for gasoline and diesel fuel for that matter (because the BTEX components are the most mobile and soluble compounds). BTEX components are in diesel fuel but in less concentrations than you would find in gasoline.

- Napthalenes and the methyl-napthalenes are also of concern in fuels.

5. Can you explain the popularity of the TPH standard?

- Its roots probably come from the water laws developed in this country. Back in the mid-80's when some of the first standards were evolving people worried about petroleum contamination of water. They worried about oil and grease so it seemed natural to look at the total contamination (TPH).

- I believe the first TPH standards came out back in '85 or '86

- it's a simple and cheap technique

a. Where was the standard developed?
- see above

b. What is the technical basis for the standard?

- the most widely used criteria is 100 ppm TPH

- the 100 ppm TPH standard can be traced to CA (the LUFT manual)
-- CA picked the 100 ppm TPH number so that have their sites would be below and half would be above and therefore they did not have to look at half of their sites
-- it has propagated from there

c. Is it appropriate to require cleanup of PCS to a strict TPH cleanup level? Why or why not?

- TPH may have some merit when you have fuels that do not have much BTEX in them

- If you cleanup a site to 100 ppm TPH, in most you probably have the site clean enough so that you do not have to worry about any significant health hazards (as long as the cleanup is risk based)

6. Please describe advantages and disadvantages of a TPH standard for cleanup of PCSs.

ADVANTAGES:
- it's a simple and cheap technique
- it looks at a wide range of contaminants
- some TPH number might make sense for middle distillates if the appropriate methods and risk assumptions are used

DISADVANTAGES:

- TPH does not makes sense for gasoline contamination

- When you analyze gasoline for TPH you lose a lot of the volatiles (due to evaporation) in the process

- Perhaps the biggest drawback to TPH is that the analytical procedures for TPH vary so much. It is one of my primary concerns with the use of TPH.
  - -- there are many methods used to measure TPH such as the standard procedure 418.1, the CA LUFT method (8015 modified), and many other methods in between.
  - -- The 418.1 method and even the CA method are relatively poorly written. These methods allow a lot of variability in the way that a person runs the test and the way that the results are interpreted. because of this, you may send a sample to a dozen different labs to do 418.1 and they may come up with numbers that differ by an order of magnitude or a couple of orders of magnitude for that matter.
  - -- Even the 8015 modified method allows to much variability

- You may get false positives with TPH analysis (i.e. some organic matter present in the soil may show up in the measurement)

a. Comment on use for measuring risk.

- NO,
  - -- TPH from a gasoline analysis is going to be totally different than a diesel analysis. This drawback inhibits the potential to correlate risk with TPH.

b. Comment on use for indicating contaminant mobility potential?

- TPH does not indicate mobility
  - -- there is a general correlation between the size of the hydrocarbon molecule and its mobility potential (i.e. the gasoline constituents are more mobile than the diesel constituents which are, in turn, more mobile than the heavier fuel constituents)
  - -- TPH does not differentiate between the constituents to indicate mobility

7. Please describe advantages and disadvantages of a compound specific standard for cleanup of PCSs.

ADVANTAGES:

- since almost all risk calculations are based on specific compounds it makes sense to have compound specific standards

- the numbers that you get from analyzing for specific compounds are used in fate and transport models

DISADVANTAGES:

- more expensive (the analytical tests)

a. Comment on risk considerations.

- see above

b. Comment on contaminant mobility considerations.

- see above

[What are the concerns with the longer chain hydrocarbons once the BTEX constituents are cleaned up?]

- the longer chain hydrocarbons are a lot less mobile and therefore normally present less risk from a migration potential standpoint (less soluble also).

- There is not a lot of health studies that have been done on the longer chain hydrocarbons, hence the focus on those mobile, soluble constituents which have been looked at in health studies.

- Dr. Bauman believes that focusing on cleaning up the benzene will probably be sufficient in most circumstances. Again, the other hydrocarbons are less mobile and have less of a potential to contaminate GW.

8. Is a TPH standard or compound specific standard more protective of human health from a risk standpoint? Why?

- Compound specific would be more protective because it tells you more about what the risk is (RA are based on specific chemicals)

- With TPH you do not know how much of the known hazardous chemicals are represented.

9. What indicator compounds, if any, do you feel should be used in establishing cleanup standards for PCSs?

- GASOLINE: BTEX
- MIDDLE DISTILLATES: BTEX and maybe Napthalenes
- HEAVIER FUELS: probably the PNA's because the most is known about them

- Dr. Bauman considers jet fuel a hybrid between gasoline and kerosene (1/2 gasoline - 1/2 kerosene)
    - -- jet fuel should be treated somewhere between gasoline and the middle distillates

10. Is there any other information/considerations you would recommend we look at in our research?

- I'll send you some 4 or 5 papers on TPH and risk for middle distillates

Technical Expert Interview

Contact: Dr. Paul Kostecki
Research Associate Professor
University of MASS
Managing Director for CHESS

Date of Interview: 21 May

1. Please state your name, title, and agency. Please describe your expertise and experience with petroleum contaminated soil (PCS).

- involved with PCS technical and policy issues since 1984

- from a research standpoint looking at best technology for cleanup as well as focusing in on the risk assessment portion of cleanup. Specifically, the exposure assessment through the amount of soils children ingest.

2. Comment on the importance of risk assessment in developing PCS cleanup standards or approaches.

- Dr. Kostecki believes risk assessment (RA) is important in developing PCS cleanup standards or approaches

- RA provides a tool that allows people to look at a site in the same sort of terms and develop their decision on whether to clean it up or not clean it up based on a certain set of guidelines (RA guidelines)
    - -- these guidelines are flexible enough to allow for site specific information to be brought into the decision making

- "with regards to determining the real risk and or the real dangers at a site, RA methodology is the most flexible and realistic"

- RA allows one to "tailor" the cleanup to a specific site and could, therefore, reduce the overall cost of cleanup

- when "cleanup numbers" are set they are full of conservative assumptions
    - -- all of these conservative assumptions together results in a very conservative cleanup number and because of this he believes that the majority of sites are being cleaned up to low levels

- using RA "has to be more cost effective" because you can eliminate the overly conservative assumptions and "tailor" your cleanup activities to a particular site

- "cleanup standards or numbers reduce the flexibility of decision making and make cleanup a black and white issue"

- those proponents for "cleanup numbers" argue that when you have flexibility and allow for "judgement calls", as is the case when RA is used, it adds to the time component of cleanup

-- people spend a lot of time debating/discussing why they did something this way or that way which often results in no cleanup action at all

- those in favor of "cleanup numbers" say that if there is a number you eliminate the discussion/debate involved with RA/judgement calls and therefore can more quickly move into cleanup actions

3. What risk assessment criteria are important in establishing a PCS cleanup standard? Which is most important and why?

- to have adequate health information about the constituents of the petroleum product

-- "it's important to have a good handle on the constituents of concern ..t a petroleum contaminated site"

- need a very good handle on the potential exposure routes

-- for example: if you had a gasoline spill the soil ingestion pathway would of normally little concern because of the characteristics of the BTEX components (which are considered to be the constituents of concern for gasoline). BTEX are:

--- volatile
--- soluble
--- they move in the subsurface

-- for heavier fractions like diesel: the importance of GW contamination becomes less and the soil ingestion pathway may be of more importance because of PAH's and because the heavier end distillates bind to the soil more than the gasoline or lighter end distillates

MOST IMPORTANT:

- a chemical's potential to cause harm in the event of exposure

- the potential of a hazardous chemical to reach a receptor

-- as an example: if you have something that is very hazardous in small quantities and has a high likelihood of reaching a receptor than you have a high risk

-- chemical constituents that do not move or do not go anywhere and are not hazardous should exposure occur than there would not be much risk associated with it

4. Should separate standards be established for different petroleum products (i.e. gasolines, middle distillates, diesel, heavy fuels)? Why or why not?

- I would say yes if they were done on a chemical constituent basis, but there is too much variation of what is in petroleum products (see notes at end)

- Since I feel the scientific community does not know enough about what happens in the environment to all of the constituents found in petroleum products, I would have to say NO right now

5. Can you explain the popularity of the TPH standard?

- TPH was "one of the first numbers that was out there in the literature" (100 ppm)

- people were looking for something, some guidance

- the engineers and the lawyers love it because it is a number (concrete)

a. Where was the standard developed?

- the 100 ppm TPH standard was developed in New Jersey

b. What is the technical basis for the standard?

- Stokeman and Dime article (see critique in book Petroleum Contaminate Soils)

[Please comment on the Stokeman and Dime research.]

- many gaping holes in the Stokeman and Dime RA

- Stokeman and Dime used the chemical constituents in a virgin product, but that changes immediately once a product is spilled

- Stokeman and Dime used one type of gasoline (there is a lot of variation in gasoline throughout the country)

- Stokeman and Dime used benz(o)pyrene as a surrogate PAH but Dr. Kostecki is not sure that is the most accurate way of doing it

- Stokeman and Dime used soil ingestion data that was not the most accurate at the time

c. Is it appropriate to require cleanup of PCS to a strict TPH cleanup level? Why or why not?

- no, because there is no health basis for TPH and the problems with the analysis of TPH for different types of petroleum products are to great

6. Please describe advantages and disadvantages of a TPH standard for cleanup of PCSs.

ADVANTAGES:

- "its a number"

- "people believe that is takes a broad cut at the chemicals that are there"

DISADVANTAGES:

- "it is not necessarily a realistic cut or a representative cut at the chemicals that are there"

- the amount of TPH in soils can vary based on the petroleum product, site specific characteristics. time it has been there

- there are difficulties in determining what you are actually measuring:
  -- "a TPH measurement by one methodology isn't the same as a another type of method--you'd be looking at different ends of the spectrum depending on the type of analytical method

a. Comment on use for measuring risk.

- a TPH number tells you nothing about risk associated with the soil--there is no health basis
  -- as an example: a 100 ppm TPH measurement at a fresh site may have 9 ppm of benzene contributing to the 100, but a 100 ppm measurement at a weathered site may only have 1 ppm of benzene contributing to the 100 ppm

b. Comment on use for indicating contaminant mobility potential?

- a TPH measurement does not tell you anything about the contaminant mobility potential (the differences between the constituents would tell you this)

7. Please describe advantages and disadvantages of a compound specific standard for cleanup of PCSs.

ADVANTAGES:

- allows you to concentrate on the "bad actors"

DISADVANTAGES:

- for some fuels it is still a debate as to what compounds are representative of the mixture

a. Comment on risk considerations.

- from a risk perspective, those compounds that are hazardous and are relatively mobile should be focused in on

b. Comment on contaminant mobility considerations.

- there are certain constituents that are relatively mobile and if GW contamination is of concern then it may be appropriate to focus on these constituents

- there are, however, some compounds found in the heavier fraction products that are not relatively mobile yet may be of concern if soil ingestion is a concern

8. Is a TPH standard or compound specific standard more protective of human health from a risk standpoint? Why?

- "a compound specific standard is certainly more protective" because a compound specific standard is more accurate than a TPH standard

9. What indicator compounds, if any, do you feel should be used in establishing cleanup standards for PCSs?

- an indicator compound in gasoline (as afar as mobility) is MTBE. MTBE almost always leads the contamination plume
  - -- MTBE indicates that the contaminant is gasoline
  - -- MTBE does not indicate risk however (compared to benzene there is less hazard associated with it than with benzene)

- you have to be careful when talking about indicator compounds. Indicator compounds can be used to indicate mobility, what the contaminant is, and hazard.

- for diesels or heavier fuels it should probably be the PAH's, such as naphthalene, benz(o)pyrene

- Dr. Kostecki has seen literature saying that diesel fuel has no BTEX and other literature saying 7% BTEX were found in some diesel samples

10. Is there any other information/considerations you would recommend we look at in our research?

POTENTIAL EXPERTS TO TALK TO:

1. Bruce Bauman at API
2. Dr. Ray Laoer: Univ of Texas at Austin

Chairman of Scientific Advisory Board for the EPA

3. Dr. Jim Dragon: Dragon Corp., Senior Editor of AYAHS Journal
   phone: 313-932-0228 FAX: 313-932-0618
4. Dr. Tim Potter: UMASS Analytical Chemist
   phone: 413-545-3505 FAX: 413-545-5910

FURTHER NOTES:

- the variability of the chemical constituent data available on petroleum products makes it difficult to identify (with certainty) those chemicals that represent the hazard associated with the whole mixture
  - -- the info on gasoline and the research done on gasoline allows the most confidence (of any petroleum product) in identifying the surrogate components representing the risk of gasoline mixtures--BTEX

- there is not enough known chemically about other fuels such as diesel fuel and certainly not enough known about the fate and transport of such fuels

- Dr. Kostecki suggests talking to the editor of <u>Soils</u> magazine about publishing the results of our thesis in the Dec '93 issue
  - -- Susan Parker is the editor (816-254-8735)

Technical Expert (Air Force) Interview

21 Jun 93

Contact: Lt Col Ross Miller
Chief, Technology Transfer Division
Air Force Center for Environmental Excellence

2. What are Air Force concerns regarding the standards used for cleanup of petroleum comtaminated soils (PCSs)?

- The concern is that if a cleanup standard is based on TPH, the standard has no substance. The TPH standard was developed as a screening standard. It makes reasonable sense to use it as a screening standard to give an indication that BTEX might be present, but it makes no sense as a cleanup standard because the TPH standard was based on BTEX from the beginning.

- There might be a better standard than BTEX. But, it is clear that the TPH standard is based on a BTEX standard.

- [We have identified concerns from some regulators that the makeup of petroleum is extremely variable and that if TPH is left in the ground, there may be some compounds other than BTEX that would present risk. Could you comment on this?]

- John Wilson, EPA, said that before we are ever going to get rid of the TPH standard we are going to have to do more toxicological studies on TPH. There is a proposed Air Force project at Tyndal AFB to do this. This is going to be a very difficult study. The question is the compounds and levels used to conduct bioasseys: when there is no BTEX left, no heptane left, or no dodane left? At what point are you going to do this? You can see that you very rapidly get to such as large study that you wouldn't be able to reach any conclusions. A possibility is to do a BTEX and a non-BTEX mixture and compare them.

- Again, everyone has evolved into using a TPH standard. There are concerns that there might be compounds in petroleum that present risk which we are not aware of, but in fact it was developed from a BTEX standard. There is no reasonable reason to believe that there are substances in petroleum more toxic that the BTEXs, or probably even of the same order of magnitude of toxicity. If you take some the compounds that they have data on and look at the LD50's, you can see that the straight chained hydrocarbons just aren't toxic in the same order of magnitude as the aromatics.

- If you get rid of the BTEX, on the surface at least, it looks like the site will be reasonably clean.

- TPH is an over-conservative approach due to lack of knowledge.

3. Can you provide the history behind the Air Force's concerns in the standards used for cleanup of PCSs?

- Lt Col Miller initiated these concerns with his paper that will be published in the Military Engineer. The paper has been approved for publication.

4. What historical and/or current trends can you identify in regulatory requirements for cleanup of PCS (i.e. negotiation of cleanup requirements)?

- This whole problem, from what you're finding [regarding flexibility in the state standards and provisions for conducting risk assessments] may be more of a perception problem and lack of Air Force personnel being fully in formed on their options. So they are just launching out on the 100 ppm TPH standard.

- When I go and talk and ask the question about who is being held to a 100 ppm standard, ninety percent of the hands in the room go up. It may very well be that the people that you are talking to, at that level, have the latitude to make decisions based on risk. But the people that are dealing with our bases don't. So they are using 100 ppm.

- I think you've identified the major trend, that regulators are looking more at risk. Although this is the official party line, I'm not sure that this is happening in practice. I'm not sure where the breakdown is. My suspicion is that it is a lack of understanding with our base folks with how much flexibility they have with the regulation.

- Everybody, when I ask the question says that they are still going to 100 ppm TPH. That's the general answer. There are people that say they look at BTEX, but there are very few that look at it by itself.

- **[Do you feel the best way to go with this is to have some sort of modelling program that can be used to establish set criteria?]** There are a lot of vadose zone type models that one can use to predict BTEX leaching from soils to groundwater. We've taken the approach with bioventing that we are going to go out and remove the BTEX. An existing vadose zone model could then be used to say at what point we are safe. These points have been established. If we accept the fact that the work that California did is adequate then those safe levels in soil have already been established. If we achieve those, I think we've done all we really need to do.

- Plus, what we are finding is that there is not much BTEX left in the majority of our sites. If the BTEX is gone and the risk is gone, we should not be touching these sites. We should not even be bioventing them. We are finding a lot of sites that are oxygenated all the way to the water table already. We are backing off and saying bioventing is not going to do any good here, let nature take its course. At these sites there is no BTEX; it is gone and is nondetectable (in the soils anyway).

- What you'll find however, is that the soils analysis is not the best. You can get a lot of nondetects in soils, but you'll still have some BTEX in soil gas. I've got one case were I've got non-detect in soil and 900 ppm in soil gas.

- If BTEX is good indicator and so are volitale compounds, we should be characterizing sites based on soil gas, install bioventing systems and treating them. When soil gas reaches a predetermined level, we should quit. We should forget the soil sampling. We'll spend more money doing sampling then cleaning the sites.

- **[I assume you mean the lighter fractions of petroleum, how about the heavier fractions of petroleum?]** Again, we can use a fate and transport model, but we know what happens. PAH's don't move. The heavier aliphatics have extremely low solubility. So, if you use the same process that they used to establish safe levels of BTEX in soils, we would find much higher levels of these compounds would be acceptable. Then you have the other complicating factor that there is no (or limited) toxicity data on n-decane or do-decane.

- **[Would you advocate a standard based on PNA's]** No! Because what is the pathway? We have a viable, plausible pathway with BTEX to groundwater and groundwater to human consumption. We are just grasping if we use a PAH standard where we assume an ingestion pathway. The ingestion pathway is not appropriate! I don't think that a PAH standard makes any sense.

- If you read the California LUFT manual, the reason that they come up with a TPH standard is so that you can have a quick and dirty indication of whether there is BTEX there. If there is no BTEX in the soil samples all the way the water table, the site should be closed because it presents no risk to groundwater (assuming the ingestion pathway is insignificant).

5. Please describe advantages and disadvantages of a using TPH standard for cleanup of PCSs

- There is a huge disadvantage beyond the risk aspects. The method "sucks", generally speaking. If you use a method 418.1 for TPH the concoction that the method requires that you put together has virtually no similarity to what we find at our petroleum sites. To give you a good example, we established a calibration curve using the method concoction, then we made a calibration curve out of 30 weight oil, just like the oil that contaminates our soil. The calibration curves were different; by a lot. The method makes no sense.

- Then you have to look at what you've got when you're done. TPH doesn't mean anything.

- The only advantage of a TPH standard is money, and that is why they established the standard to begin with. Really, if there is no TPH then there is a chance that there is no BTEX. Thus, screening for TPH would preclude you from wasting the money from doing a BTEX sample using 8010/8020 or whatever. If there is TPH, what that means is that you should go sample for BTEX. You should not infer a BTEX level, based on a TPH level because there is no way to do it.

- The intent [of using TPH] was to take soil out underneath a tank and if the TPH was at a certain level then you probably have a BTEX problem somewhere else. That was it; and we shouldn't read anymore into it than that.

6. Please describe advantages and disadvantages of a compound specific standard (such as BTEX) for cleanup of PCSs.

- Advantage is that when you have a number, you have a number that means something. You have toxicological data that is associated with those compounds and you can do a risk assessment based on those numbers.

- The disadvantage is that it costs a little more to do it.

7. Do you feel there would be cost savings associated with a compound specific standard verses a TPH standard?

- No question. And the reasons are simple: we can clean it up faster (we know), and if we take it one step further and get rid of the soil sampling, we can save a whole bunch of money there.

- [At several Air Force sites] Out of 42 datapoints, we had 19 sites with BTEX levels less than 10 ppm. If you look at the state standards, a number of states are using a total BTEX standard of 10 ppm. These numbers are before bioventing. A number of states have a standard for benzene at 1 ppm. Out of the 42, 38 had benzene concentrations less than 1 ppm. If benzene is the indicator compound, this indicates that we don't have a problem. This is the good news. The bad news is that many of the sites that have soil concentrations less than 1 ppm, have soil gas concentrations in the hundreds (ppm). This calls into question the method used.

- If we have a big enough data set, we can take it to the regulators and say look: "we can go out there and close a bunch of these sites based on soil samples, but we know there is benzene there in certain concentrations from soil gas, why don't you let us be more conservative and evaluate our sites based on soil gas." Then we could run out and do soil gas surveys which are cheap and fast. If there is significant soil gas benzene, we vacuum it for a while until its gone... and that's it. It is a clean site... done. And you avoid the huge cost of soil samples. We're talking major dollars here. One hundred to two hundred million dollars is not an over-estimate of the cost implications.

- This is not the total picture. It's also risk based. If someone comes back to us and says that do-decane is toxic at certain levels, then we have to re-look. But, we should not be the people having to prove the toxicity of every compound in fuels. We are taking the ones that we know are the most toxic, know are the most mobile, and make the most sense to be indicator compounds. And if we remove these to safe levels, then that should be it. So its better from a public health standpoint because we have the real number, and have looked at it, and know what's there, and it's much better from a cost standpoint.

- We [the Air Force] likes to emphasize the risk side.

8. Other considerations

- With regards to bioventing, data from Engineering Science is going to Battelle. Battelle is putting the data into the form we want and is putting together the design manual and running the statistics. We need to get their data sheets. One of Major Miller's charts is a chart showing BTEX divided by TPH times 100. This shows the percent BTEX in TPH (which is essentially what we are doing).

- Talk to Andrea Leason (614) 424-5942 [will be in on Thursday]. She will sent the spreadsheet she uses to generate the graphs. We can request directly from her. This will be a dynamic database where data will constantly be added. Currently there are 35 sites in the database.

- Work that might be productive: call regulators in the states that we interviewed and ask them about their cleanup standards. See if they have the same interpretation of flexibility.

- [Do you think there would be more costs associated with performing a risk assessment at every site] I am not suggesting that we have to do a risk assessment at every site. I'm suggesting that if our soil reaches a BTEX level that has already been determined to be safe that it should be enough. I'm not suggesting that we have to run a fate and transport model at every site to show what's going to happen with our BTEX.

- Because even if it hits the groundwater then we have the next step; the natural attenuation in the groundwater. We are saying that type of work will have to have a risk assessment, because we know it will be required in order to sell it. But that will not be based on BTEX in soil, it will be based on BTEX in water.

- I've heard the side of the argument that it is cheaper to clean up to a 100 ppm TPH standard than to go through the hassle of doing a risk assessment. I am not suggesting that we have to do that either. If we have risk assessments and modelling from a select number of sites in different states that have established a BTEX standard, that should be adequate.

Technical Expert Interview:

Date of Interview: 27 May 1993

Contact: Dr. Thomas Potter
Director of the Mass Spectrometry Facility
Univ of Mass
Amherst, MA

1. Please state your name, title, and agency. Please describe your expertise and experience with petroleum contaminated soil (PCS).

EDUCATION:

- B.S. in Chemistry from **UMAINE** (*go BLACK BEARS!*)
- M.S. in Soils Science from Cornell University
- PhD awarded by UMASS at Amherst

WORK HISTORY:

- approx. 12 years of experience in working in the analysis of petroleum in the environment which included:
  - -- 5 years as a Regulator (Director of Organic Chemical Analysis Laboratories for the State of Maine)
  - -- research work at UMASS involving environmental fate of gasoline and developing "novel" measurements for residues of gasoline and other petroleum hydrocarbons in soil and water
  - -- consultant and expert witness in many cases involving the environmental release of petroleum

2. Comment on the importance of risk assessment in developing PCS cleanup standards or approaches.

- "I thing the process of risk assessment and risk assessing contaminants in environmental media are of fundamental importance in developing meaningful standards."

[Do you think RA is needed for every contamination site or do you think that a generic RA, where a universal standard can be applied to all sites, is more appropriate?]

- having worked for a regulatory agency, I would have to say that the simplest and most direct approach is establish a uniform standard and apply it to the community at large (all individuals or corporate entities who may be responsible parties)

- technically, there is certainly an argument that could be made that uniform standards are inappropriate and that some form of a RA should be applied to each and every site to determine what is an appropriate or acceptable that could be permitted to remain on a particular site

3. What risk assessment criteria are important in establishing a PCS cleanup standard? Which is most important and why?

- "Fundamentally, the issue is exposure." The potential for exposure needs to be evaluated.
  -- built into exposure are all sorts of information requirements that includes:
    --- amount and types of contaminants present in various media as well as assessing local geologic, geologic, climatic factors which allow those contaminants to be transported thus result in exposure through air, soils, water, etc.

- the toxicology of the contaminants must be investigated and examined in considerable detail (once exposure has occurred what are the effects)--I am speaking from the perspective as an analytical chemist and a soil scientist when I emphasize measurement characterization and/or transport environmental fate

- in other words, the hazard associated with the contamination and its ability to reach a receptor are the important criteria

[Do you think there is enough information available in the literature to identify surrogate constituents in all petroleum products?]

- "I feel that there is a body of information available that could be used to make more informed assessments of risk." I believe that there is more research that is necessary. Better measurements could be made which would allow people performing RA's to make more informed judgements about the risks from environmental releases. The key to measuring is to realize that the product is changing (because of migration, biodegradation, etc.) once it is released into the environment.

[Please comment on the variability in petroleum product composition.]

- in my experience the variability is not a confounding factor because of the other uncertainties in RA

- for gasoline, the BTEX constituents are the fundamental materials that need to be risk assessed based on their toxicity--the other constituents's relative toxicity is far less based on my knowledge of the published literature

[Do you think that there are indicator compounds in diesel and jet fuel that can be used with confidence in RA?]

- No. I do not believe that diesel and jet fuel have been that effectively characterized. My best guess is that the naphthalene group (including akylated-napthalenes) of compounds would be the most appropriate for RA based upon their relatively high concentrations and their perceived toxicity for the middle distillates.

4. Should separate standards be established for different petroleum products (i.e. gasolines, middle distillates, diesel, heavy fuels)? Why or why not?

- No. I do not think there should be some uniform standard that treats each fuel generically. Rather, I think we should look at some specific fraction of the fuels. It would be my opinion that the aromatics fraction of the fuels need to be taken into account in terms of setting a standard. And also when the standard is set some direct measurement of the contaminants present in the contaminated media and should be required.

[Do think TPH adequately measures aromatics in soil?]

- It doesn't differentiate between materials which are aromatic or paraffinic (sp?). It says they are petroleum hydrocarbons and treats all petroleum hydrocarbons equally. More is known about the aromatics and from an exposure perspective the aromatics are more soluble in water than the other components of fuel. The logic for measuring aromatics is compelling for two reasons:

(1) toxicity

(2) environmental fate/mobility--aromatics are mobile and can contaminate GW

5. Can you explain the popularity of the TPH standard?

- it mystifies me...

a. Where was the standard developed?

- I have heard that the original TPH soil contamination standards came from NJ and was based on a very simplistic RA that was done at a time that a standard was needed.

- I attribute the use of TPH to the lack of leadership from the EPA (particularly in the 1980's). The EPA said that petroleum hydrocarbons are a state issue and let each and every state formulate their own policy.

b. What is the technical basis for the standard?

- see above

c. Is it appropriate to require cleanup of PCS to a strict TPH cleanup level? Why or why not?

- No, because of the uncertainty in the data both in terms of RA and in terms of analytical measurement.

- For example, method 418.1 is a direct measurement of the paraffinic hydrocarbons in the petroleum hydrocarbons extractable from the soils. With this method, there is no direct measurement of the aromatic hydrocarbons. The assumption is made that the environmentally recovered hydrocarbon mixture proportionally has the same composition as the standard mixture that is prepared in the laboratory. In order for this measurement to be valid this is required. Because of this, there is an inherent variability to this measurement method (possibly by a factor of 2 or more). This could add to the cost of cleanup.

6. Please describe advantages and disadvantages of a TPH standard for cleanup of PCSs.

ADVANTAGES:

- People know what it is
- there are relatively simple and low cost methods for making TPH measurements

DISADVANTAGES:

- A major disadvantage is that when using TPH you are essentially characterizing all petroleum hydrocarbons as being the same in terms of their environmental hazard such as water contamination potential and/or toxicity of individual compounds.

a. Comment on use for measuring risk.

- TPH adds a lot of uncertainty to the RA. You could use it in RA but the uncertainty could go both ways (i.e. the risk could be more or less of what is estimated).

b. Comment on use for indicating contaminant mobility potential?

- If using 418.1 it doesn't really give you any real indication of mobility or leaching potential

- If using one of the Gas Chromatic based methods (8015, 8020, etc.), you may have <u>some</u> indication of the mobility potential if the data is recorded in such a way that you get a boiling point distribution of the hydrocarbon mixture. You can make the general inference that the lower the boiling point of the mixture or the lower the distillation range of the hydrocarbon mixture the more environmentally mobile it is. This assumption has limitations also such as...

(1) protection of GW--you must look at the aromatics

7. Please describe advantages and disadvantages of a compound specific standard for cleanup of PCSs.

ADVANTAGES:

- Making the process much more direct (i.e. focusing on individual constituents) is the main advantage.

- When GW contamination is of concern, the focus should be on those constituents that are relatively soluble

DISADVANTAGES:

- Fuel composition is variable and certain constituents are introduced into the fuel stream over time (such as MTBE) which need to be taken into account. RA and standards need to keep pace with what is happening in the petroleum industry in terms of the types of products that are being delivered in the market place.

a. Comment on risk considerations.

b. Comment on contaminant mobility considerations.

8. Is a TPH standard or compound specific standard more protective of human health from a risk standpoint? Why?

- In general my experience tells me that the TPH standards are more conservative. They are not necessarily more protective of human health because TPH does not tell you exactly which petroleum hydrocarbons are present. TPH has the potential to be more protective of human health but more information is needed to be sure.

9. What indicator compounds, if any, do you feel should be used in establishing cleanup standards for PCSs?

- Gasoline: BTEX compounds as well as the oxygenates (MTBE)
  (the high solubility of MTBE makes it important)

- middle distillates: (a lot more uncertainty with these fuels)
  -- (jet fuels, diesel, home heating fuels, etc.)
  -- the napthalenes represent the major constituents in the aromatic fraction
  -- also the methyl groups are of concern

- heating oils: I believe there needs to be some concern for the nitrogen and as well as oxygen containing aromatics compounds

10. Is there any other information/considerations you would recommend we look at in our research?

- I think you should look very critically at the analytical methods that are used for measuring TPH (418.1 or the 8015 type methods) and look at just what exactly those measurements measure and just what they do not measure.

- I'll send you a copy of studies by some German groups on middle distillate products and their aromatic fractions.

- Check the fuel characterization laboratories at Wright-Patterson AFB.

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Vita

Captain Rick A. Blaisdell was born on 3 March 1965 in South Paris, Maine. He graduated from Lewiston High School in Lewiston, Maine in 1983. He attended the University of Maine in Orono, Maine where he earned a Bachelor of Science degree in Electrical Engineering in December 1987. As a member of the Reserve Officer Training Corps, he was commissioned into the United States Air Force upon graduation. Captain Blaisdell was initially assigned to the 379th Civil Engineering Squadron, Wurtsmith AFB, Michigan as a Design Engineer. He later become the Chief of Heavy Repair and the Chief of the Readiness Branch. As officer-in-charge of the squadron Prime Base Emergency Force Team, he led them to Jeddah, Saudi Arabia during Operation DESERT STORM. He entered the Engineering and Environmental Management Program, School of Engineering, Air Force Institute of Technology in May 1992. Upon graduation in September 1993, he will be assigned to the 647th Civil Engineering Squadron, Hanscom AFB, Massachusetts.

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Vita

Captain Mark E. Smallwood was born on 6 July 1961 in San Francisco, California. He graduated from Tulane University in May 1986 with a Bachelor of Science in Civil Engineering. As a member of the Reserve Officer Training Corps, he was commissioned into the United States Air Force upon graduation. Capt Smallwood held positions as Assistant Chief, Bioenvironmental Engineering, at Norton AFB, CA and Kadena AB Japan. In 1990, he was assigned to the Air Force Center for Environmental Excellence, Brooks AFB, as a technical project manager. He was chosen to enter the Graduate Engineering and Environmental Management program, School of Engineering, Air Force Institute of Technology, in May 1992. Upon graduation in September 1993, he will be assigned to the Headquarters Air Force Base Disposal Agency, Washington, D.C.

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Evaluation of the Total Petroleum Hydrocarbon Standard at Jet Fuel Contaminated Air Force Sites

Selection of Possible Scientifically-Based Alternatives

Prepared by
EA® Engineering, Science, and Technology, Inc.
For
Armstrong Laboratory
Environmental Sciences Branch
Occupational and Environmental Health Directorate
Brooks AFB, Texas

January 1994

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EXECUTIVE SUMMARY

A study was conducted to examine potential substitutions for total petroleum hydrocarbons (TPH) at JP-4 (jet fuel) contaminated Air Force installations. The objective of the study was to examine the scientific basis for potential use of compounds other than TPH in establishing cleanup standards at JP-4 sites. There were four steps to the study's analytical approach:

(1) Examination of current bases for existing numerical soil cleanup levels for TPH and four major fuel constituents —— BTEX (benzene, ethylbenzene, toluene, and xylene);

(2) Identification of potential TPH substitutes for establishing soil cleanup concentrations;

(3) Selection of the most appropriate TPH substitute; and,

(4) Options for raising a risk-based soil cleanup concentration for the TPH substitute (*i.e.*, benzene).

(1) *Current bases for existing numerical soil cleanup levels*

There are four categories of methods being used by states to establish cleanup concentrations:

- A minimally scientifically-defensible approach, yielding semi-site-specific cleanup concentrations, based on ground water protection;
- A scientifically-defensible approach, yielding site-specific cleanup concentrations, protective of ground water;
- A risk assessment approach with varying degrees of scientific defensibility, typically yielding soil cleanup concentrations with variable extents of health protection from a soil ingestion route; and,
- Scientifically-defensible approaches, with site-dependent methodologies, yielding highly site-specific cleanup concentrations, ultimately protective of ground water.

The general categorization of the bases for BTEX and TPH cleanup concentrations showed that all state-specific approaches could be described as scientifically-based, technology-driven, or other (*e.g.*, "cleanup to background" policy). In summary,

- There are no federal soil cleanup criteria established by the USEPA for TPH, or for BTEX, *per se*.

- There are state-specific cleanup concentrations for TPH and BTEX.
- The majority of state-specific BTEX cleanup concentrations are human health-protective.
- The majority of human health-protective cleanup concentrations are designed to be protective of ground water for use as drinking water.

(2) *Identification of potential TPH substitutes for establishing soil cleanup concentrations*

A series of criteria were used to judge the viability of JP-4 constituents as TPH substitutes. These included chemical fate and transport[1], toxicity[2], and regulatory standards for relevant media of concern.[3]

Fate and transport. The fate and transport properties of principal candidates for TPH substitutes can be summarized in the following manner. In a new JP-4 spill, BTEX and lower molecular-weight alkane substitutes[4] are the volatile constituents. Given their lower molecular-weights, relatively higher water solubilities, and greater soil mobilities, these constituents tend to leach into soil with surface water precipitation and migrate over greater vertical distances than the other potential substitutes.

The primary fate of PAHs, which do not volatilize and tend to remain associated with soils, appears to be biodegradation, although the nature and extent of this activity will vary widely with such factors as the size of the spill, the soil type, and soil microbial characteristics. Transport of higher molecular-weight PAHs associated with jet fuels[5] is limited by their soil affinity and low water solubility. These compounds are increasingly hydrophobic in nature and tend to remain preferentially associated with the organic carbon fraction in soil, as opposed to the percolating water phase. Lower molecular-weight PAHs, such as fluorene, have been shown to exhibit faster migration rates than their higher molecular-weight counterparts and are most likely to reach the water table.

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[1] Relative proportions of potential substitutes in JP-4, physicochemical properties, temporal variations in soil-related distributions of potential substitutes, and implications for human routes of exposure.

[2] Substitute-specific toxic effects, availability of relevant toxicity information, and availability of established, recognized toxicity benchmark values.

[3] Identification of existing or anticipated media of concern and availability of established standards for media of concern in addition to soil (*i.e.*, groundwater maximum contaminant levels [MCLs]).

[4] *e.g.*, hexane, octane, and, cyclohexane

[5] *e.g.*, percolation or leaching of benzo(*e*)pyrene, chrysene, and fluoranthene

Naphthalene and substituted naphthalenes, by virtue of their smaller size and greater relative water solubility, are also expected to be transported further, although perhaps not as rapidly as the BTEX and alkanes.

Therefore, higher molecular-weight PAHs and possibly some naphthalene would appear to remain associated with the soils at the site of the spill for significantly longer periods of time than BTEX, while BTEX, naphthalene, and low molecular-weight PAHs would be anticipated to migrate further, thereby exhibiting a greater potential for ground water contamination.

Toxicity. A comparison of the magnitude of the toxicity values for the carcinogenic JP-4 constituents (oral slope factors for benzene and chrysene indicates that the marginally larger slope factor is associated with chrysene [(0.073 $(mg/kg/day)^{-1}$ for chrysene; 0.029 $(mg/kg/day)^{-1}$ for benzene]). However, at this time benzene is the only potential TPH substitute with an oral slope factor established by the USEPA.

Comparisons of the noncarcinogenic toxicity values for potential TPH substitutes indicate that the lowest chronic oral R_fDs and, hence, the greatest potential for producing adverse health effects under similar exposure conditions, are for naphthalene and several of the PAHs.

(3) *Selection of the most appropriate TPH substitute*

The physicochemical properties of benzene influencing its potential for ground water impact, the magnitude of and scientific understanding of its toxicity, and an established toxicity value, combine to support benzene as the TPH substitute of choice for JP-4. Chrysene, the sole carcinogenic PAH in JP-4, as a possible substitute is not as viable a substitute, given its less definitive toxicity benchmark concentration and lesser potential to impact ground water. Naphthalene is not a viable choice, given the lesser magnitude of the toxicity associated with naphthalene, the lack of an established toxicity benchmark concentration, and the lack of a maximum contaminant level (MCL). Coupled with the anticipated lack of carcinogenic PAHs in ground water, the inability to accurately extrapolate noncarcinogenic toxicity information, and the absence of additional MCLs for PAHs other than benzo(*a*)pyrene, *the TPH substitute of choice is benzene.*

(4) *Options for raising a risk-based soil cleanup concentration for the TPH substitute (i.e., benzene)*

Factors that affect the benzene cleanup level[6] were explored. As benzene carcinogenicity is anticipated to drive the site risk estimates, the two major components specifically examined were alternative cancer slope factor (SF) determinations for benzene (*i.e.*, distributional analysis of

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[6] (1) The predetermined "acceptable" level of risk, (2) benchmark measures of toxicity, and (3) site-specific exposure parameters.

dose-response relationships developed from cancer studies), and site-specific exposure strategies (*i.e.*, distributional analysis of exposure estimates) that might be employed at Air Force JP-4 sites.

Alternative cancer slope factor (SF) determinations. Based on the current USEPA documentation on the derivation of the benzene SF (USEPA 1985), the potential for appreciably altering the benzene cancer SF is not anticipated to be significant, based on three strengths of the existing SF:

- Unlike the majority of chemicals for which SFs have been derived, the benzene cancer SF was estimated from existing human epidemiology data.
- The benzene cancer SF was estimated using two different lifetime cancer risk models (relative and absolute risk) and two different assumptions of the appropriate exposure parameters (cumulative and weighted-cumulative exposure).
- The benzene SF was presented as the geometric mean of the maximum likelihood estimates (MLEs), as opposed to the more standard approach used for the majority of SFs, which is to present the SF as the 95th percentile upper bound.

In addition, a recent study designed to quantitatively re-evaluate the USEPA estimate of the benzene SF proposed that the benzene cancer SF could effectively be decreased by an order of magnitude. However, the USEPA is indicating that there has been no study to substantially refute the currently established SF.

Site-specific exposure reduction strategies. The potential for exposure of humans who come in contact with the site of a former JP-4 spill can be influenced by identification of the current and future land uses at the site, identification of the human receptor of greatest concern, physical nature of the site, the size/volume of the spill, and the age of the spill. The need for site-specific considerations and the use of site-specific exposure parameters, whenever feasible, is crucial to this process.

With regard to values placed on the various exposure parameters, an alternative approach to the use of conservative assumptions is an exposure distributional analysis, in which ranges or distributions of individual exposure parameters (*e.g.*, the distribution of adult body weights) are considered to produce an overall distribution of potential exposure. In exposure assessment, Monte Carlo simulation can be used to estimate distributions for exposure assumptions, rather than point estimates. Use of this methodology does not alter the basic structure of the exposure estimate and further refines the way chemical intakes are calculated.

Conclusions

- There is no established USEPA regulatory policy for BTEX or TPH soil cleanup concentrations, to date. There are variable state-specific approaches to setting BTEX and/or TPH soil cleanup levels.

- State-specific soil cleanup concentrations for BTEX are based primarily on protection of human health via protection of ground water, and/or protection of health for the soil ingestion route.

- Among all potential substitutes for TPH at JP-4 spill sites, benzene appears to be the most appropriate substitute based on its toxicity (carcinogenicity), weight-of-evidence cancer classification (Category A carcinogen), motility in the environment, ubiquity at JP-4-contaminated sites, and potential for migration to ground water.

- Based on these parameters, risk-based soil cleanup concentrations based on BTEX tend to be driven by benzene. Risks associated with exposure to benzene in ground water used as a drinking water source is anticipated to dominate risks for benzene in other media.

- There is no scientific consensus on use of specific distributions. However, scientifically defensible, rationally chosen, site-specific distributions should be used to estimate exposure.

Recommendations

- Benzene should be adopted as the TPH substitute.

- Research and funding efforts should focus on formulating site-specific soil cleanup concentrations for benzene, based on protection of ground water.

- A cost-benefit analysis should be undertaken for soil remediation of benzene and TPH, using current, acceptable remediation methods, and applying a site-specific approach.

- Research and funding efforts should be directed towards characterizing TPH, including chemical characterization, health effects, fate and transport, and the utility of TPH in the risk assessment process.

SECTION SUMMARIES

Section 1: Background and Rationale for Seeking Alternatives to TPH at JP-4 Contaminated Sites

Section 1 of this report introduces the concept of replacing total petroleum hydrocarbons (TPH) as the basis for establishing cleanup concentrations of JP-4 chemical constituents in soil at individual Air Force bases. There are two reasons why replacing a TPH-based cleanup standard is desirable: (1) the chemical composition of TPH, as a class of chemicals, is poorly and inconsistently defined, and (2) the TPH-based cleanup standard is often based solely on the detection limit of current analytical equipment, so that there is no rational scientific basis, such as human health protection, for the standard. In this investigation, alternative JP-4 constituents are examined as potential TPH replacements in a sequential, stepwise fashion by: (1) surveying the different ways that governments (federal and state) use TPH to set standards, (2) identifying potential chemical candidates that are reasonable alternatives to TPH, (3) examining the most promising candidate substitutes in depth for their scientific merit, (4) selecting from among these chemicals the best TPH substitute, and (5) quantifying the impact of choosing this best substitute on the cleanup standard. Via this process, attention quickly turns to BTEX (benzene, toluene, ethylbenzene, and xylene) as the most promising chemical group, and finally to benzene as the most promising chemical substitute for TPH in establishing a cleanup standard.

Section 2: Current Bases for Existing Numerical Soil Cleanup Levels for TPH and BTEX

Section 2 of this report identifies, as the first step in examining substitutes for TPH, how federal and state governments are currently regulating soil cleanup of JP-4 chemicals —— specifically what the soil cleanup requirements are and how they were derived. The purposes of this step are to: (1) determine the extent to which the governments rely on TPH to establish a cleanup standard, (2) what quantitative and qualitative criteria are used to set the TPH standard, (3) whether other chemicals, such as benzene, are considered at all (and if so in what way), (4) the consistencies among and differences between various governments in establishing cleanup standards, (5) identification of states that might be amenable to considering alternatives to TPH as a basis for establishing cleanup, and (6) the adaptability of government criteria to other chemicals that are promising TPH substitutes. The results of this survey were used to assist in selecting promising TPH substitutes.

Section 3: Potential TPH Substitutes for Establishing Soil Cleanup Concentrations

In Section 3 of this report, constituents in JP-4 are considered for their suitability as TPH substitutes as the basis for soil cleanup standards. Four classes of chemicals were short-listed because, as groups, they are present in JP-4 in greater proportions than other chemicals: BTEX, napthalenes, alkanes, and PAHs. Chemicals in these four groups were examined in depth according to their environmental fate and transport, toxicity, and existing regulatory standards. While other JP-4 constituents may have one or more desirable qualities as TPH substitutes, their lower proportions in JP-4 blends and lesser importance as soil contaminants removed them from in-depth consideration. **Section 3.0** presents and compares the comprehensive information available on JP-4 constituents without drawing conclusions about the most suitable TPH substitute. Conclusions about the most promising JP-4 substitutes and selection of the preferred substitute are deferred for detailed consideration in **Section 4.0.**

Section 4: Selection of the Appropriate TPH Substitute(s)

Section 4 uses all of the information compiled and assessed in **Sections 2.0 and 3.0** to select the preferred TPH substitute. As explained in **Section 1.0**, the desire is to select a standard that is both scientifically defensible and based on human health risk, rather than on best available technology. **Section 4.0** describes the health risk assessment process and how it leads to the development of a preliminary remediation goal (PRG) for soil cleanup. Specific chemicals in the four chemical groups identified in **Section 3.0** (BTEX, naphthalenes, PAHs, and alkanes) were then considered in the context of human health risk and the development of a soil PRG. To do this, the following criteria were considered: toxicity, availability of toxicity benchmark values, the calculated PRGs, anticipated environmental fate and transport, potential for contaminating other environmental media, and relevance of state-specific approaches to regulating soil contaminants. Based on these criteria, benzene was selected as the preferred TPH substitute.

Section 5: Options for Raising a Risk-Based Soil Cleanup Concentration for the TPH Substitute (Benzene)

Section 5 is focussed on how an appropriate preliminary remediation goal (PRG) is developed for benzene, the preferred TPH substitute in soil as determined in **Section 4.0**. The two key elements considered in establishing the benzene PRG are the same two key elements used to establish human health risk: benzene's cancer potency factor and, quantitative expression of the potential for human exposure to benzene. Various ways of expressing both of these elements were explored in this section, including the use of Monte Carlo simulation. PRGs are site-specific because many of the factors used to calculate them vary from site to site and are necessarily dependent on conditions at a particular site. Therefore, site-specific PRGs were not calculated in **Section 5.0.**

Section 6: Conclusions and Recommendations

Section 6 of this report presents the conclusions which constitute the results of analyses performed throughout this report. Additionally, Recommendations are also presented which are the outcome of the conclusions of these analyses as well as additional considerations.

1.0 BACKGROUND AND RATIONALE FOR SEEKING ALTERNATIVES TO TPH AT JP-4 CONTAMINATED SITES

Summary: ***Section 1.0*** *of this report introduces the concept of replacing total petroleum hydrocarbons (TPH) as the basis for establishing cleanup concentrations of JP-4 chemical constituents in soil at individual Air Force bases. There are two reasons why replacing a TPH-based cleanup standard is desirable: (1) the chemical composition of TPH, as a class of chemicals, is poorly and inconsistently defined, and (2) the TPH-based cleanup standard is often based solely on the detection limit of current analytical equipment, so that there is no rational scientific basis, such as human health protection, for the standard. In this investigation, alternative JP-4 constituents are examined as potential TPH replacements in a sequential, stepwise fashion by: (1) surveying the different ways that governments (federal and state) use TPH to set standards, (2) identifying potential chemical candidates that are reasonable alternatives to TPH, (3) examining the most promising candidate substitutes in depth for their scientific merit, (4) selecting from among these chemicals the best TPH substitute, and (5) quantifying the impact of choosing this best substitute on the cleanup standard. Via this process, attention quickly turns to BTEX (benzene, toluene, ethylbenzene, and xylene) as the most promising chemical group, and finally to benzene as the most promising chemical substitute for TPH in establishing a cleanup standard.*

Historically, there are numerous sites on Air Force installations, at which jet fuel spills have occurred or can be anticipated to occur. As part of the Installation Restoration Program, military installations are required to delineate and remediate concentrations of fuel-related contaminants in site media whose concentrations exceed existing state and/or federal standards. Sources of controversy and uncertainty in the extent of remediation required stem from the lack of a scientific, credible basis for establishing the applicable standards or guidance criteria, real or perceived. This document contains an exploration of the scientific or technological basis for setting cleanup concentrations or guidance criteria for fuel spill-related compounds, in particular for JP-4 jet fuel contaminants.

Traditionally, the typical fuel spill-related indicator compounds for which cleanup concentrations have been established are the total petroleum hydrocarbons (TPH), and the four BTEX (benzene, toluene, ethylbenzene and xylene) compounds. The analytical progression followed in this exploration was based on six assumptions:

1. Anticipation that the federal and state regulatory contexts for these indicator chemicals can be characterized.

2. Specific approaches that the federal and state governments are using (or will use in the future) to formulate regulations on cleanup standards (TPH or otherwise) can be assessed.

3. The scientific rigor with which existing standards have been established can be assessed and characterized.

4. Individual JP-4 fuel-related chemicals, if carefully selected and justified, can serve as a basis for the development of cleanup standards that are alternatives to the TPH standard.

5. An opinion can be rendered on the relative merit of a benzene-based cleanup standard as an alternative to the TPH cleanup standard.

6. Uncertainty associated with a benzene-based cleanup concentration can be measured.

With these assumptions in mind, and recognizing that the TPH cleanup standard is technology-based, the overall objective of this study is:

> *To examine the scientific rationale for potential use of compounds OTHER than TPH, based on human health criteria rather than technology-based criteria, in establishing cleanup standards at JP-4 contaminated Air Force installations.*

The scope of the analyses presented in this report can be summarized in five sequential stages contained in the following sections of this document:

2.0 Current Bases For Existing Numerical Cleanup Levels for TPH and BTEX
3.0 Potential TPH Substitutes for Establishing Soil Cleanup Concentrations
4.0 Selection of the Appropriate TPH Substitute(s)
5.0 Options For Raising a Risk-based Soil Cleanup Concentration For the TPH Substitute (Benzene)
6.0 Conclusions and Recommendations

2.0 CURRENT BASES FOR EXISTING NUMERICAL SOIL CLEANUP LEVELS FOR TPH AND BTEX

Summary: Section 2.0 of this report identifies, as the first step in examining substitutes for TPH, how federal and state governments are currently regulating soil cleanup of JP-4 chemicals —— specifically what the soil cleanup requirements are and how they were derived. The purposes of this step are to: (1) determine the extent to which the governments rely on TPH to establish a cleanup standard, (2) what quantitative and qualitative criteria are used to set the TPH standard, (3) whether other chemicals, such as benzene, are considered at all (and if so in what way), (4) the consistencies among and differences between various governments in establishing cleanup standards, (5) identification of states that might be amenable to considering alternatives to TPH as a basis for establishing cleanup, and (6) the adaptability of government criteria to other chemicals that are promising TPH substitutes. The results of this survey were used to assist in selecting promising TPH substitutes.

The four BTEX compounds were chosen, in addition to TPH, for characterization of existing state and federal soil remediation concentrations because:

- They are associated with fuel spills;
- They are ubiquitous;
- Their environmental fate and transport is predictable;
- Their toxicology is relatively well-characterized; and,
- There is regulatory precedence at federal and state levels for establishing site-specific cleanups based on one or more component(s) of BTEX.

2.1 Regulatory Approaches for Soil Remediation of TPH and BTEX

The range of state and federal regulatory approaches for establishing site-specific cleanup concentrations was established in order to:

- Obtain a sense of the feasibility, locally and nationally, of moving individual states and the U.S. as a whole away from a technology-driven cleanup concentration for TPH to a more scientifically defensible risk-based cleanup concentration for BTEX;
- Identify reasonable criteria that can be used to justify replacing TPH with BTEX;

- Ascertain the proportion of states relying on TPH to establish cleanup concentrations and the proportion relying on additional or other criteria; and,
- Assume a broad reach in examining alternative cleanup bases for all Air Force installations, distributed throughout the entire U.S.

In an effort to determine the approaches that are being taken towards formulating and enforcing soil remediation levels for fuel spill-related contaminants such as TPH and BTEX, state-specific information was compiled from numerous sources in the literature, as well as via direct telephone conversations with state agency representatives. Information on the federal approach towards regulating these constituents was obtained via direct telephone contact with USEPA representatives involved in ongoing efforts.

2.1.1 Federal Approaches to Establishing Soil Remediation Concentrations for Fuel-Spill Related Contaminants

To date, the USEPA has not proposed standards for soil remediation of TPH or BTEX compounds. For example, the USEPA's Underground Storage Tank (UST) program has decided not to develop federal guidelines for the cleanup of soils contaminated with TPH/BTEX. Rather, UST is leaving the selection of TPH/BTEX soil cleanup levels at the discretion of individual states (John Heffelfinger, personal communication, 1993). For states desiring guidance, UST will provide information on other states' TPH/BTEX activities. In addition, UST is funding an effort to summarize all state activities in TPH/BTEX soil cleanup; study results will appear in Soils Magazine (Debbie Tremblay, personal communication, 1993).

The USEPA's Office of Solid Waste and Superfund Office have assembled a Work Group whose purpose is to develop a set of soil screening levels for 30 contaminants (including the BTEX compounds). The screening levels would be used by USEPA during investigation of NPL (National Priorities List) sites. If a contaminant soil level at a site exceeds the screening level, further investigation and characterization of the site would be recommended.

The Work Group is developing a tiered approach to deriving soil screening concentrations (Loren Henning, personal communication, 1993). The following information describes a tiering process proposed by the Work Group. It should be noted that this proposed method may be revised prior to the issuance of any Work Group guidance documents. A first tier, generic, conservative soil contaminant level would be calculated (this level would equate to a soil concentration that would not result in the exceedance of groundwater standards - either health-based National Primary Drinking Water Regulations (MCLs), or state-specific groundwater standards). The generic level may be determined using a partitioning/dilution/attenuation factor equation with default values. A second tier soil screening level may use the same equation, with site-specific data rather than default values. Third and fourth tiers might include a leach test and full site-specific characterization, respectively. It is assumed that screening levels based on successively higher tiers will be progressively less conservative (*i.e.*, higher soil concentrations will result).

The Work Group's Draft Interim Guidance Document is currently undergoing internal review at the USEPA. The Document is not likely to be available until at least June, 1994 (Loren Henning, personal communication, 1993).

2.1.2 State Approaches to Establishing Soil Remediation Concentrations for Fuel Spill-Related Contaminants

Information pertaining to the existing regulations or guidance criteria for TPH and BTEX was sought for a subset of states perceived to be representative of the variation in remediation levels and approaches for all states. The bases for existing regulations were ascertained from relevant sources in the literature, state guidance documents, or personal contacts. Any information pertaining to proposed or ongoing approaches was solicited as well. The following sections discuss the strategy for identification and selection of target states, and the state-specific characterizations of regulatory standards and approaches.

2.1.2.1 Identification of Soil Cleanup Concentrations of BTEX and TPH for Targeted States

A national survey, conducted by Bell *et al.* (1991), was initially used to compile regulatory approaches used by states to clean up hydrocarbon-contaminated soils, particularly from leaking underground storage tanks. Based on these survey results, certain state-specific considerations in the establishment of numerical values for cleanup concentrations were identified, including background levels of TPH/BTEX, land use of the site, ground water proximity, and potential for ground water impacts. All parameters were subsequently compiled for each state, as presented for BTEX/TPH-specific data in **Table 2-1**. The information in **Table 2-1** is based primarily on examination of the existing survey information (Bell *et al.* 1991) and preliminary personal communications with members of select state agencies.

2.1.2.1.1 Selection of Targeted States for Further Evaluation

From the compilation of state regulatory approaches based on the published Bell *et al.* (1991) survey, 26 states were identified as warranting further investigation to determine the bases for the BTEX/TPH cleanup levels, as illustrated in **Figure 2-1**. The following initial criteria were used to select the target states:

- States with the highest cleanup concentrations from the reported spectrum of levels (*e.g.*, Tennessee, Georgia);

- States with the midpoint cleanup concentrations from the reported spectrum of levels (*e.g.*, Idaho, Washington);

- States with the lowest cleanup concentrations (or cleanup to background) from the reported spectrum of levels (*e.g.*, Ohio, Minnesota, Illinois); and,

- States that historically have exhibited environmental leadership, innovation, or conservative environmental policy (*e.g.*, California's enactment of Proposition 65).

This approach to targeting states for more in-depth delineation of regulatory approaches was based on three assumptions:

- Inclusion of the complete range of numerical values would reflect the range of approaches being used by the states;

- All relevant parameters considered by the states in establishing values would also be encompassed; and,

- Inclusion of states with historically progressive environmental practices would "flag" any new trends or developments in establishing remediation criteria.

2.1.2.1.2 Compilation of Information from Targeted States

State-specific information for the final 26 targeted states was categorized as mentioned above. For each targeted state, additional or supplemental information was subsequently sought by contacting state regulatory agencies and soliciting verbal or written documentation for the numerical values for TPH/BTEX, as well as the bases for these values. State-specific categories reflect the parameters specifically considered by the states in their methods for deriving the numerical values. If current policy differed from prior survey information, or if clarification of state-specific parameters being considered in the establishment of numerical values was obtained, the state-specific information was adjusted accordingly. The updated and adjusted regulatory information for the 26 targeted states is presented for BTEX in **Table 2-2** (and detailed in **Appendix A**). A similar table was generated for TPH concentrations and analytical method considerations. This information is presented in **Table 2-3**. States which allow development of site-specific cleanup concentrations were not listed with definitive cleanup concentrations in the tables. A comprehensive series of footnotes were compiled for each table. Readers should refer to them for more detail on the relevant categories and exceptions therein.

2.1.2.2 Characterization of State Approaches to Establishing Cleanup Concentrations for BTEX and TPH

There were four overriding, common themes observed on examination of the approaches and methodologies used by the 26 targeted states in establishing soil cleanup concentrations for BTEX:

(1) Most states sought to protect the quality of ground water. Whether fate-and-transport models or "generic" attenuation factors were used, background levels applied, or technology-based cleanup plans utilized, soil standards were established such that ground water quality would be in compliance with some existing ground water quality standard.

(2) The underlying goal of most state hydrocarbon cleanup policies is the protection of human health. The ground water standards mentioned above were almost without exception drinking water standards when potable water was impacted. Usually the standard invoked was the federal maximum contaminant level (MCL) under the National Primary Drinking Water Regulations (NPDWRs), but occasionally a state-specific drinking water standard was cited.

(3) The overwhelming trend in establishing soil cleanup concentrations is to use quantitative, compound-specific, scientifically defensible methodologies. Quantitative human health risk assessment is playing an increasingly important role in the derivation of compound-specific cleanup levels.

(4) States acknowledged the limitations of using a TPH cleanup level. Five states did not regulate TPH (Hawaii, Illinois, Michigan, New Jersey, and New York), two used TPH levels only as screening levels or to provide "rough" estimates of the degree of contamination (Massachusetts and Oregon), and one state alluded to plans to include phasing out use of TPH altogether (New Hampshire). This amounts to approximately 30 percent of the targeted states that do not rely on TPH measurements for soil cleanup.

There is considerable variation among the states with respect to approaches and methodologies. For instance, some states permit the use of different standards, applied on a site-by-site basis, based on site-specific information. Others apply fairly consistent criteria to most sites. Certain states advocate the use of very conservative assumptions in their risk-based approaches, while others allow or encourage the use of site-specific assumptions. Still other states allow the responsible party to select an approach for establishing a cleanup concentration, based on consideration of several available options and economic factors, provided that mutual accord is reached. Regardless of the exact nature of the methods, the overriding concerns were centered on human health protection, particularly by achieving relevant ground water standards.

In addition to variation in states' approaches and methodologies, there are varying degrees of scientific rigor employed by states in establishing cleanup standards.

(1) *A minimally scientifically defensible approach, yielding semi-site-specific cleanup concentrations, based on ground water protection*

Typically, these states used methods that considered "typical" background concentrations and/or basic attenuation and migration assumptions to formulate semi-site-specific cleanup values. These values were to be protective of ground water quality, and usually included several levels of stringency in their derivation. The states surveyed employing this approach are Colorado, Georgia, Hawaii (for BTEX only), Idaho, Kansas (for BTEX only), Massachusetts (for TPH only), Missouri, Ohio, Oregon (for TPH only), South Dakota (for TPH only), and Tennessee.

(2) *A scientifically defensible approach, yielding site-specific cleanup concentrations, protective of ground water*

This included states that apply fate and transport computer modeling methods and site-specific characteristics to determine levels of soil contamination corresponding to "acceptable" levels of hydrocarbons in ground water. States surveyed which adopted this approach are California, Illinois (for BTEX only), Massachusetts (for BTEX only), New Hampshire, Oregon (for BTEX only), and Texas.

(3) *A risk assessment approach with varying degrees of scientific defensibility, typically yielding soil cleanup concentrations with variable extents of health protection from a soil ingestion route*

These states based cleanup concentrations on the availability of either a more conservative set of "generic" (nonsite-specific) cleanup levels or a "less conservative" (more site-specific) set of risk-based cleanup levels. Michigan (for BTEX only) and Washington were the only states surveyed using this approach.

(4) *Scientifically defensible approaches, with site-dependent methodologies, yielding highly site-specific cleanup concentrations, ultimately protective of ground water.*

States included here derive site-specific remediation goals on a site-by-site basis, usually in conjunction with a ground water monitoring program in order to ascertain that the remediation goals are met. Surveyed states which implement this approach are Delaware, Louisiana, Maryland, Minnesota (for TPH only), Utah, and Wisconsin.

The general categorization of the bases for BTEX and TPH cleanup concentration showed that all state-specific approaches could be described as:

- Scientifically-based (*e.g.*, human health risk, fate-and-transport computer modeling)
- Technology-driven (*e.g.*, BAT remediation), and

generic migration and attenuation assumptions).

The relative proportions of the 26 targeted states that base their soil cleanup values on these three general categories, *scientific*, *technology*, and *other*, are presented graphically for BTEX and TPH in **Figures 2-2 and 2-3,** respectively. The categories corresponding to a *scientific* basis or approach included use of human health risk assessment procedures, the use of fate and transport modeling, and protection of ground water to health-based MCLs with fate and transport modeling. Scientific approaches for TPH were developed by deriving criteria for one or several of the BTEX compounds, and extrapolating them to TPH, on a fuel-specific (BTEX proportionality) basis. *Technology*-based categories included concentrations based on the limits of the relevant remediation technique or the method detection limit. The general category of *other* was applied to categories which encompassed cleanup to "background", aesthetic concerns, application of such attenuation factors as soil-to-ground water dilution factors, or use of cleanup concentrations established by another state, with or without scientific justification.

Of the 24 states that have developed soil cleanup concentrations for BTEX, 17 use scientifically-based approaches for their derivation (California, Delaware, Florida, Illinois, Louisiana, Massachusetts, Michigan, New Hampshire, New Jersey, New York, Ohio, Oregon, Tennessee, Texas, Utah, Washington, and Wisconsin); one (Maryland) uses technology-driven cleanup criteria; the remaining six states (Colorado, Georgia, Hawaii, Idaho, Kansas, and Missouri) fall into the category 'other'.

Of the 21 states that have developed soil cleanup concentrations for TPH, 12 use scientifically-based approaches for their derivation (California, Delaware, Louisiana, Massachusetts, Minnesota, New Hampshire, Ohio, Tennessee, Texas, Utah, Washington, and Wisconsin); one (Maryland) uses technology-driven cleanup criteria; the remaining eight states (Colorado, Florida, Georgia, Idaho, Kansas, Missouri, Oregon, and South Dakota) fall into the category 'other'.

2.2 Summary

- The USEPA has not established federal soil cleanup criteria or TPH or for BTEX.
- There are state-specific cleanup concentrations for TPH and BTEX.
- The majority (22 out of 24) of state-specific BTEX cleanup concentrations are human health-protective. The following states have human health-protective BTEX cleanup concentrations: California, Colorado, Delaware, Florida, Hawaii, Idaho, Illinois, Kansas, Louisiana, Maryland, Massachusetts, Michigan, Missouri, New Hampshire, New Jersey, New York, Ohio, Oregon, Tennessee, Texas, Utah, and Washington.

- The majority (12 out of 22) of human health-protective cleanup concentrations are designed to be protective of ground water drinking water standards. The following states have human health-protective cleanup concentrations protective of ground water drinking water: California, Colorado, Delaware, Hawaii, Idaho, Illinois, Minnesota, Missouri, New Hampshire, New York, Utah, and Washington.

Table 2-1. Characteristics of BTEX/TPH Cleanup Levels By State (Bell, Kostecki, and Calabrese, 1991)

State	Based On: Detection Limit	Bkgd Levels	Appearance or Smell	HNu/OVA/PI	GW Proximity or Impact	Land Use	Nature of Cpd (MW)	WQ Stds	Human Health	Are Site-Specific	Other	Non-Existent	TPH	BTEX	Benzene	Toluene	Ethyl-benzene	Xylene
AK							X						50-100	10				
AL					X								100					
AR										X								
AZ								X	X				100		130	200	68	44
CA										X	X		10-10,000		0.3-1	.3-50	1-50	1-50
CO	X				X					X								
CT											X		50 (gas)					
DE												X	100 (gas)	10 (gas)				
FL				X						X			50					
GA					X								100-500	20-100				
HI					X			X	X	X			50					
IA							X			X			100					
ID					X		X						100-1000		1	1	1	1
IL			X		X									16.025	0.025			
IN										X			100					
KS													100		1.4			
KY	X	X											Bkgd	Bkgd				
LA										X								
MA				X									100					
MD	X	X																
ME				X						X			20-50					
MI	X	X							X	X			B/D/R	B/D/R				
MN				X			X						50					
MO										X			10	10				
MS					X						X		100 (dsl)	100 (gas)				
MT									X	X			100	10				
NC							X				X		10					
ND												X						
NE										X								
NH										X	X		10-100	1				
NJ											X		100					
NM				X			X						100		10			
NV					X	X	X						100					
NY											X							
OH	X	X							X	X			Bkgd	Bkgd				
OK													50	10				
OR					X						X		40-1000					
PA									X	X	X							
RI						X	X			X			50					
SC										X								
SD			X							X			10					
TN					X					X	X		100-1000	10-500				
TX					X					X			100	30				
UT										X	X		50					
VA					X				X				100					
VT				X	X					X								
WA										X	X		100-200		0.1	4	3	2
WI	X												10					
WV	X				X					X			100	100				
WY					X								10-100					

HNu/OVA/PI = HNu brand organic vapor analyzer/photoionization detector
MW = Molecular weight

Table 2-2. Derivation Methodologies for BTEX Cleanup Levels By State for 26 Target States

	Aesthetics	Remediation Technology	Analyzed Other States	Attenuation Factor	Bkgd or Detect. Limit	Fate/Transport Modeling	Human Health Risk	Completely Site-Specific	Regulatory Goal	Type of Level	Level (ppm)	Remarks
CA						•	••	•	GW,HH	RG		Use of SESOIL/AT123D
CO			•				••		GW,HH	RG	20-100 total BTEX	Importance of ground water potability
DE							••	•	GW,HH	RG		Consultants hired for derivation [1]
FL							•		HH	RG	100 total VOA	Conservative residential exposure scenario used
GA			•		•				GW,SW	CS	20-100 total BTEX	In-stream water quality drives cleanup levels
HI				•			••		GW,HH,SW	RG	1.7 B; 21 T; 1.4 X	State water quality criteria drives cleanup levels
ID			•				••		GW,HH	RG	1 B, 1 T, 1 E, 1 X	Looked at Oregon's approach
IL						•			GW	CAL	16.025 BTEX; .025 B	Apply to USTs only, not above-ground spills
KS				•			••		GW,HH	CAL	1.4 B	Cleanup level is flexible
LA								•	GW	RG		Consultants hired for derivation [1]
MA						•	•		GW,HH	RG	B 10-200; T 90-2500; E 80-500; X 500-2500	Use of SESOIL/AT123D
MD		•							GW	RG		Site remediated until GW concentrations stabilize
MI					•	•	•	•	GW,HH	CAL		RP chooses bkgd, detect. limit, or risk asst.
MN												Regulate TPH only
MO			•				••		GW,HH	RG	1 total BTEX; 0.5 B	Importance of ground water potability
NH						•	••	•	GW,HH	RG		Method based on CA LUFT procedure
NJ							•		HH	RG	.001-.013 B; .5-1 T; .1-1 E; .01-1 X	Ground water impact important
NY	•			•			•		GW,HH	RG	.001 B; .005 T; .005 E; .005 X	Must satisfy both GW and HH criteria
OH			•	•			•		GW,HH	RG	.006-.5 B; 4-12 T; 6-18 E; 28-85 X	Importance of drinking water quality
OR						•	•		GW,HH	CS	0.1 B; 80 T; 100 E; 800 X	Use of SESOIL/AT123D
SD												Regulate TPH only
TN			•	•			••	•	GW,HH	CS	10-500 total BTEX	RP may use state's levels or derive their own
TX						•	•	•	GW,HH	RG		Use of API computer model
UT							••	•	GW,HH	RG		Developed on a site-by-site basis
WA			•				•	•	HH	RG	.5 B, 40 T, 20 E, 20 X	RP chooses state's levels or risk asst.
WI								•	GW,HH	RG		Consultants hired for derivation [1]

[1] This method provides greater flexibility than choosing among risk assessment, background, or detection limit values, since the latter methods values tend to be conservative and must be approved by the state.

Aesthetics: Lack of adverse aesthetic qualities is an important consideration when considering soil to be "clean"

Remediation Technology: Soil considered "clean" when ground water concentrations achieved asymptotic levels

Analyzed Other States: Cleanup levels were determined on the basis of the levels used by other states

Attenuation Factor: Allowable concentrations in soil were determined by multiplying allowable ground water concentrations by an accepted attenuation factor (e.g., 20)

Bkgd/Detl.im: Remediation goal equals background levels (in literature or via sampling) or designated MDL

Fate/Transp: Computer model was used to calculate soil concentrations which would leave ground water concentrations below a certain level

Human Health Risk: * = Risk-based remediation goals established through use of a structured risk assessment methodology
** = Level is protective of human health in that it is protective of ground water to some drinking water standard

Site-Spec.: Remediation goals established on a case-by-case basis, using virtually any scientifically-defensible method

Reg. Goal: GW = Goal of cleanup level is protection of ground water; HH = Human Health; SW = Surface Water

Type Level: RG = Level is Remediation Goal; CS = Level is Cleanup Standard (Law); CAL = Level is Corrective Action Level

Table 2-3. Derivation Methodologies for TPH Cleanup Levels By State for 26 Target States

	Aesthetics	Remediation Technology	Analyzed Other States	Attenuation Factor	Bkgd or Detect. Limit	Fate/Transport Modeling	Human Health Risk	Completely Site-Specific	Regulatory Goal	Type of Level	Level (ppm)	Remarks
CA						•		•	GW	RG		Use of SESOIL/AT123D; derived from BTEX levels
CO			•						GW	RG	100-500	Importance of ground water potability
DE								•	GW	RG		Consultants hired for derivation
FL				•					GW	RG	10-50	Assume attenuation factor of 2
GA			•		•				GW,SW	CS	100-500	In-stream water quality drives cleanup levels
HI												Regulate BTEX only
ID			•						GW	RG	100-1000	Looked at Oregon's approach especially
IL												Regulate BTEX only
KS					•				GW	CAL	100	Cleanup level is flexible
LA								•	GW	RG		Consultants hired for derivation
MA						•			GW,HH	RG	500-2500	Use of SESOIL/AT123D; derived from BTEX levels
MD		•							GW	RG		Site remediated until GW concentrations stabilize
MI												Regulate BTEX only
MN								•	GW,SW	RG		Consultants hired for derivation
MO			•						GW	RG	10	Importance of ground water potability
NH						•		•	GW	RG		Method based on CA LUFT procedure
NJ												Regulate BTEX only
NY												Regulate BTEX only
OH			•	•			•		GW,HH	RG	105-1156	Importance of drinking water quality
OR				•					GW,HH	CS	40-1000	Use of EPA attenuation factor of 100
SD			•	•					GW	RG	10-100	Used conservative attenuation factor of 1-10
TN			•	•				•	GW	CS	100-1000	RP may use state's levels or derive their own
TX						•	•	•	GW,HH	RG		Use of API computer model
UT								•	GW	RG		Established on a case-by-case basis
WA			•				•	•	HH	RG	100-200	RP chooses state's levels or risk asst.
WI								•	GW,HH	RG		Consultants hired for derivation

Footnotes for Table 2-2 apply; except no MCLs apply for TPH so there will be no ** in Human Health Risk column

Figure 2-1. Selection of Targeted States

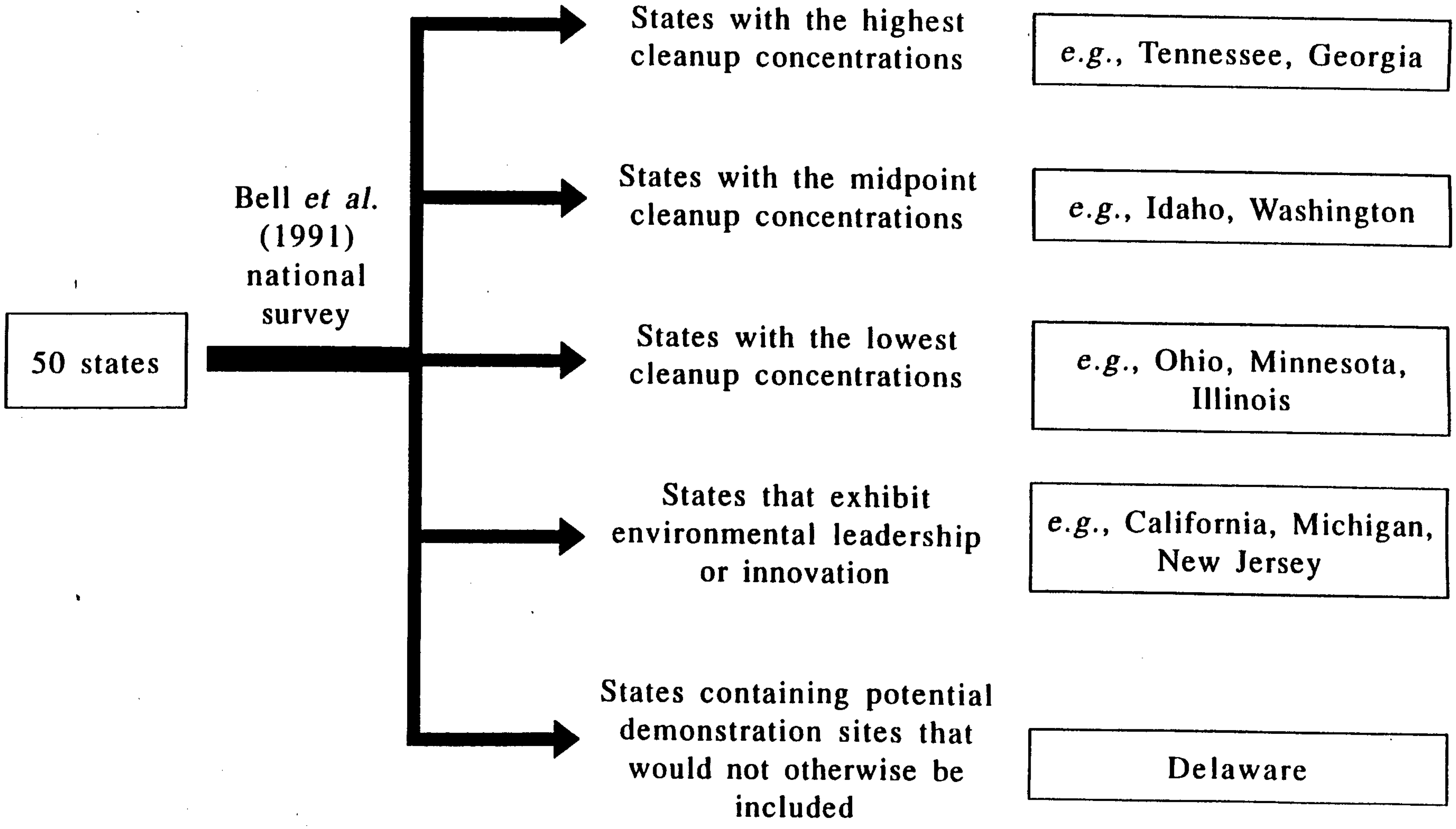
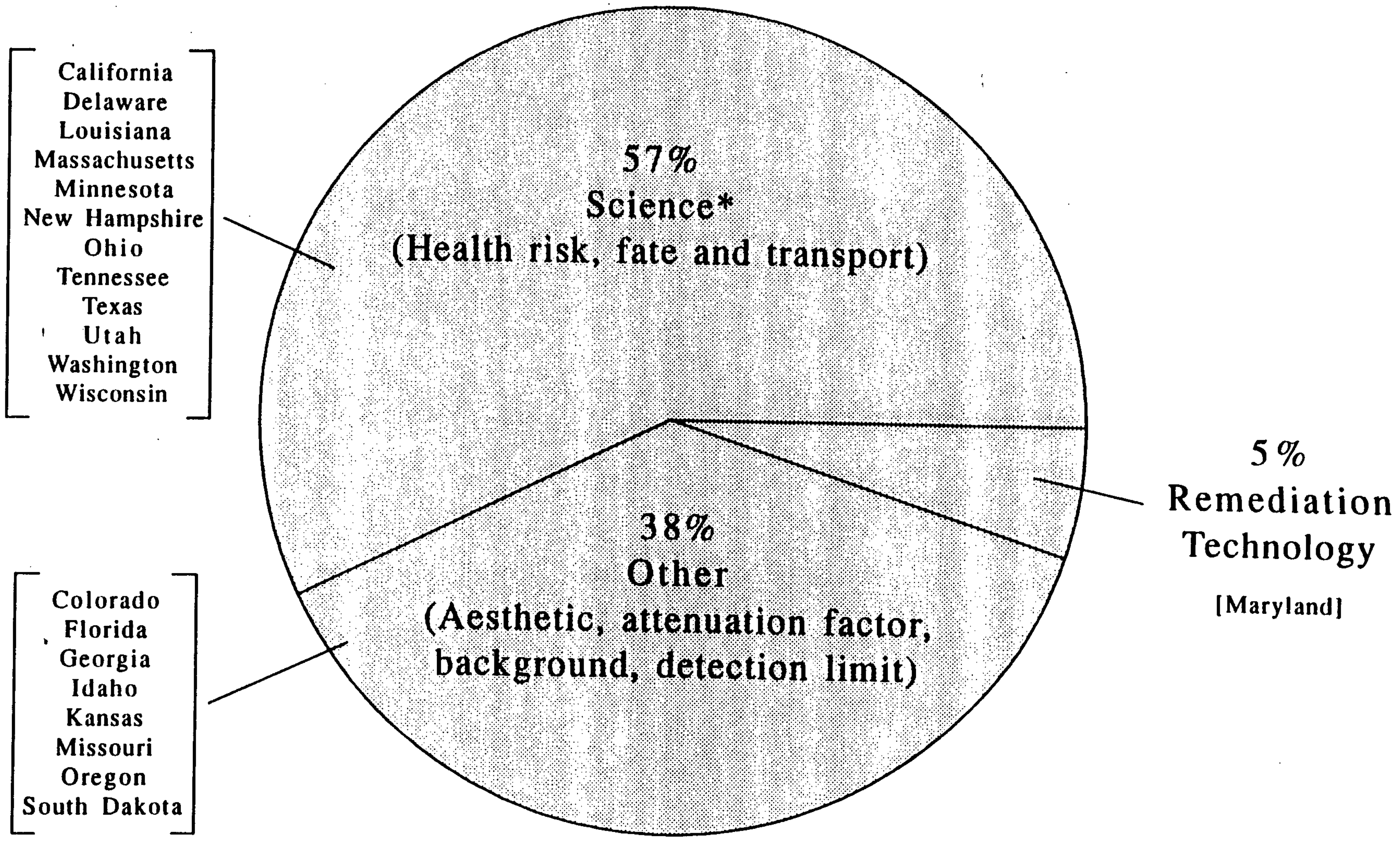
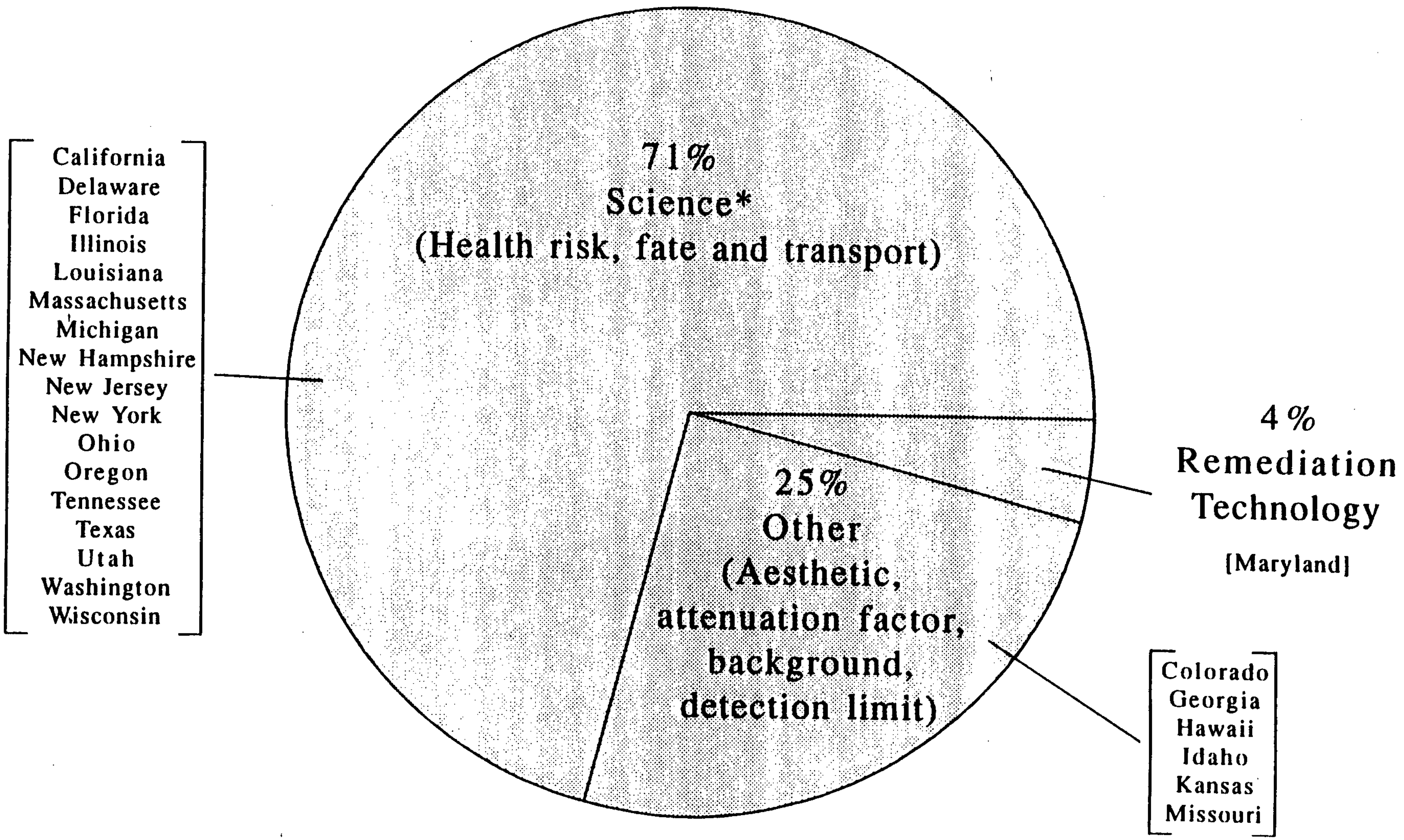


Figure 2-2. Target State-Specific Bases for TPH Soil Cleanup Concentrations



*Cleanup concentrations are not based on TPH-related science, per se. They tend to be based on BTEX, with extrapolation to TPH concentrations for specific fuels.

Figure 2-3. Target State-Specific Bases for BTEX Soil Cleanup Concentrations



*Of the 17 states using a science-based approach, 12 states have regulatory goals designed for groundwater protection

3.0 POTENTIAL TPH SUBSTITUTES FOR ESTABLISHING SOIL CLEANUP CONCENTRATIONS

*Summary: In **Section 3.0**, constituents in JP-4 are considered for their suitability as TPH substitutes as the basis for soil cleanup standards. Four classes of chemicals were short-listed because, as groups, they are present in JP-4 in greater proportions than other chemicals: BTEX, napthalenes, alkanes, and PAHs. Chemicals in these four groups were examined in depth according to their environmental fate and transport, toxicity, and existing regulatory standards. While other JP-4 constituents may have one or more desirable qualities as TPH substitutes, their lower proportions in JP-4 blends and lesser importance as soil contaminants removed them from in-depth consideration. **Section 3.0** presents and compares the comprehensive information available on JP-4 constituents without drawing conclusions about the most suitable TPH substitute. Conclusions about the most promising JP-4 substitutes and selection of the preferred substitute are deferred for detailed consideration in **Section 4.0**.*

The potential for specific constituents of JP-4 fuel to serve as TPH substitutes was investigated, specifically for the purpose of exploring their usefulness in formulating JP-4 representative soil cleanup concentrations. The soil medium was used here because it is the medium of choice by regulators for TPH cleanup at most sites. The analysis was conducted using a three-step approach:

(1) fate and transport considerations;

(2) assessment of toxicity; and,

(3) determination of the existence of regulatory standards for the media of concern.

These considerations can be used to assist in the identification of the appropriate TPH substitute.

3.1 Criteria for Assessing and Selecting TPH Substitutes

Multiple considerations are involved in identifying potential TPH substitutes and subsequently evaluating their relative utility in developing risk-based cleanup concentrations. The parameters considered within each of the three broad steps listed above are detailed below, and are discussed both generally and specifically for identified potential substitutes in the following sections.

Fate and transport

- Relative proportions of potential substitutes in JP-4
- Physicochemical properties

- Temporal variations in soil-related distributions of potential substitutes, and
- Implications for human routes of exposure

Toxicity

- Substitute-specific toxic effects
- Availability of relevant toxicity information, and
- Availability of established, recognized toxicity benchmark values

Regulatory standards for relevant media of concern

- Identification of existing or anticipated media of concern, and
- Availability of established standards for media of concern in addition to soil (*i.e.*, ground water MCLs).

3.1.1 Fate and Transport

There are two primary fate and transport parameters that influence the selection of a potential TPH substitute for determining soil cleanup levels. The substitute should: (1) be present in JP-4 fuels in detectable concentrations in environmental media, and (2) possess physicochemical properties that promote migration through the subsurface. Fate and transport processes are not only chemical-specific, but site-specific, as well (*i.e.*, surface and subsurface characteristics at a site influence how JP-4 constituents will segregate within and between site media over time). In this section, the chemical-specific parameters influencing fate and transport are presented.

3.1.1.1 Amounts of Potential TPH Substitutes in JP-4 or Related Fuels

JP-4 is a broad cut, naphtha jet fuel, similar to fuel oil no. 1 (kerosene), whose composition has been described as a mixture approximately 65% gasoline and 35% light petroleum distillates (Curl and O'Connell 1977). The blending of JP-4 fuel is designed to produce a product with a composition that broadly segregates (by weight) as: 32% *n*-alkanes, 31% branched alkanes, 16% cycloalkanes, 18% benzenes and alkylbenzenes, and 3% naphthalenes[7] (ATSDR 1992a). Therefore, alkanes and cycloalkanes account for the substantial portion of JP-4 fuel, followed in priority order by benzene and alkylbenzenes, and naphthalenes. Given the imprecise nature and extent of characterization of the constituents of jet fuels, these weight percents are only representative estimates. The compositional variations of specific compounds within these broad classifications are augmented by the natural variations in the compositions of the crude oil precursors to the final refined fuel (namely, crude petroleum oils or crude shale oils), as well as the refining process operated by the individual fuel manufacturers (ATSDR 1992a). Therefore,

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[7] For purposes of this report, naphthalenes are defined as group of compounds, substituted and unsubstituted, that have two fused rings. Naphthalenes fall within a larger class of compounds in JP-4, PAHs, that have multiple fused rings.

it is not possible to determine the exact concentrations of individual chemicals within JP-4 or related fuels. However, ranges of values have been generated based on available compositional information for various jet fuels or similar fuel types. In addition to these broadly grouped classes of components stated above, jet fuels such as JP-4 contain polyaromatic hydrocarbons (PAHs), although their combined weight fraction is typically less than the naphthalenes. PAHs in jet fuels tend to group within the lower molecular-weight range for these compounds (USEPA 1980).

Table 3-1 identifies the relative concentrations of the BTEX compounds within JP-4 or similar fuels. Similar information for other primary components of JP-4 and related fuels is shown in **Table 3-2**. Fuels chosen to approximate the constituents of JP-4 included low sulfur Jet fuel A, high sulfur Jet fuel A, and a more generic Jet fuel. The compositions of kerosene or fuel oil no. 1 were used only as sources of fallback information, where JP-4 or jet fuel-specific information for select compounds was not available.

As stated above, the greatest weighted proportion of JP-4 constituents includes alkanes, benzenes, and naphthalenes, with minimal amounts of low molecular-weight PAHs.

3.1.1.2 Physicochemical Properties of Potential TPH Substitutes

Certain compounds will preferentially remain associated with the site soils, while others will tend to migrate through soils with percolating surface water (*e.g.*, precipitation), and still others will fall somewhere between these two fate and transport trends. Physicochemical factors that can influence the fate and transport of compounds include:

- The potential for volatilization (*e.g.*, boiling point, vapor pressure, Henry's law constant)
- The potential to migrate through the soil column (*e.g.*, octanol-water partition coefficient (K_{ow}), molecular weight, water solubility, soil adsorption (K_{oc}))

Compounds expected to have high soil mobility would typically include those with low boiling points, high vapor pressures, and high Henry's law constants, low octanol-water partition coefficients, low molecular weights, high water solubility, and low organic-carbon partition coefficients. Conversely, compounds with relatively low soil mobility would include those having higher boiling points, lower vapor pressures, Henry's law constants, high octanol-water partition coefficients, high molecular weights, low water solubility, and higher organic-carbon partition coefficients. Chemical-specific properties for TPH substitutes, BTEX and others, are listed in **Table 3-3**. The following subsections discuss substitute-specific characteristics.

3.1.1.3 Fate and Transport of Potential TPH Substitutes

BTEX, naphthalene, alkanes, and discrete PAHs have been found in association with one or more environmental media following JP-4 fuel spills or leaks (ATSDR 1992a). Quantitative estimates of site associations have not been made. Potential TPH substitutes fall into three categories: volatile, semivolatile, and nonvolatile. The potential TPH substitutes that are generally considered to be volatile in nature include the BTEX compounds, the low molecular-weight alkanes, and naphthalenes. After a JP-4 spill or leak, the primary fate of the volatile constituents, including potential substitutes such as BTEX and some of the lower molecular weight alkanes (*e.g.*, hexane, heptane), is to evaporate. Although the majority of studies aimed at determining extent of JP-4 volatilization were conducted for JP-4 spills or leaks to water, high volatilization rates (ATSDR 1992a) after a fresh JP-4 spill on soil would also be expected for these components. These constituents of JP-4 are also typically very mobile in soils, a fact supported by the results of petroleum products and water partitioning studies (ATSDR 1992a; Coleman *et al.* 1984; Kramer and Hayes 1987) and borne out by the historical association of benzene, ethylbenzene, and toluene with ground water in the United States (ATSDR 1990a, 1992b, 1993; Coleman *et al.* 1984; USEPA 1990).

For the semivolatile to nonvolatile constituents, such as certain members of the PAH group, this is not the case. Of the PAHs, the lower molecular-weight compounds such as chrysene and fluorene have been shown to be the more mobile components. Higher molecular-weight PAHs are present in relatively small quantities compared to other constituents in JP-4 and similar fuels. In addition, as PAHs' molecular weights increase, there is a general corresponding increase in hydrophobicity. Therefore, higher molecular-weight PAHs would tend to remain associated with organic carbon fraction of soils near the site of contamination, as opposed to the percolating water phase. The combination of PAHs' physicochemical properties (low water solubility, low volatility, and high octanol-water and organic carbon partition coefficients) and relatively small quantities in fuel indicate that these compounds are not likely to be major contributors to human health risk. A synposis of how potential TPH substitutes partition in environmental media is presented in **Figure 3-1**.

3.1.1.3.1 Temporal Alterations in Substitute Distributions

For the more volatile substitutes, such as BTEX, naphthalenes, and low molecular-weight alkanes, the portions of these JP-4 components not volatilized after the initial spill event(s) will enter the surficial and near-surficial soils. Continued emissions over time may continue, albeit at lower rates, given the dilution and percolation incurred by precipitation. The smaller, less hydrophobic compounds, with relatively greater water solubilities (*i.e.*, BTEX, naphthalene, and fluorene) will migrate with percolating water, and therefore have the greatest potential for existing in subsurface soils and for impacting ground water over time.

Temporal variations in soil concentrations for the relatively nonvolatile substitutes, such as higher molecular-weight PAHs or long-chain and branched alkanes will be much less pronounced.

These PAHs appear to remain preferentially associated with the soil at the site of a spill for significantly longer periods of time than the BTEX components. Although the primary fate of PAHs in soils appears to be biodegradation (ATSDR 1990b), the actual nature and extent of biodegradation will vary widely with such site-specific factors as the size of the spill, the soil type, and the microbes present. It is anticipated that the hydrophobic and bulky alkanes would exhibit similar characteristics in the soil matrix. As mentioned above, lower molecular-weight PAHs such as fluorene (ATSDR 1992a) have been shown to exhibit faster migration rates and greater migration distances than their high molecular-weight counterparts (ATSDR 1992a), and would be more likely to reach the watertable.

The anticipated progression of alterations in the media-specific distributions of potential substitutes, as a function of increasing age of the spill (*weathering*), is qualitatively described in **Table 3-4**.

3.1.1.4 Effects of Fate and Transport on Human Exposure Routes

Variations in the distribution of JP-4 constituents in site media will influence the relative concentrations of potential TPH substitutes present over time. Information on temporal variations can be used to predict the concentrations of JP-4 fuel constituents in various subsurface media. This information can be combined with constituent toxicity information in order to determine which compounds have the greatest risks associated with them. Such compounds can be expected to be the *risk drivers* for the site. While anticipated risk drivers can be identified based on consideration of exposure routes, temporal variations, and toxicity considerations, it is site-specific features which allow for definitive determination of the compounds driving risk. The extent to which temporal effects influence the final risk drivers associated with a spill site is *emphatically* site-specific; responsible remediation decisions should be based predominantly on site-specific, not generic, information. However, it is still possible to make scientifically informed and defensible predictions, based on applicable principles and chemical properties.

Soil-to-Ground Water Fate and Transport

Variation in soil concentrations of BTEX and other potential TPH substitutes over time (*e.g.*, with increasing time-from-spill) impact the potential for one or several compounds to be the pivotal risk-driver associated with JP-4 spills. Any factor causing temporal alteration in soil or air concentrations can influence which fuel constituent will become the risk driver for routes of exposure which may include ingestion of surface soil or inhalation of vapors. However, the emerging trend towards regulating soil levels based on ground water protection may supersede exposures via soil ingestion or vapor inhalation for those compounds which present greater soil mobility (*e.g.*, BTEX, naphthalene, low molecular-weight PAHs such as fluorene). For relatively non-mobile substitutes, or substitutes lacking established ground water protective concentrations, risks from exposures via soil ingestion or inhalation may still predominate at the site.

Given the comparatively higher soil mobility of the BTEX compounds, naphthalene, and low molecular-weight PAHs, these compounds could be expected to impact ground water to the greatest extent, and within relatively shorter time spans. However, it is primarily site-specific characteristics that have the greatest potential to influence contaminant fate and transport from subsurface soil to ground water. Properties such as the magnitude of precipitation, permeability of the soil, type of soil (fraction of organic carbon present), geological strata, distance to ground water, and the physical and dynamic nature of the underlying ground water aquifer(s) will exert great influence on the subsequent fate and transport of any contaminant over time.

Illustrative Example. In a residential setting, a child playing in the surface soil at an older spill site will breathe air, and may ingest soil and ground water. The surface soil is not likely to contain volatiles, given their propensity to volatilize or migrate downward into soil over time. For the same reasons, inhalation of volatile compounds will probably not be a primary route of exposure at an older spill site. Ingestion of semivolatile, less mobile substitutes (*i.e.*, high molecular-weight alkanes or bulkier PAHs) in surface soil is more likely to occur, given their greater propensity to associate with soils. The potential risks from drinking site ground water may drive the risk for more volatile, mobile compounds. Even at a recent spill site, where migration of compounds to ground water may not yet have occurred, the typical future land use scenario involving drinking of site ground water should still address risks from this exposure route.

3.1.2 Toxicity

Criteria that must be considered in the selection of potential TPH substitutes, in addition to fate and transport properties, include an assessment of the toxicity, if any, associated with each potential substitute. The nature and magnitude of the toxic effects should be identified, and the weight-of-evidence in the literature supporting these effects verified. In order to apply a risk-based approach to formulating cleanup concentrations, the existence of any established, recognized, toxicity benchmark values for each compound must be verified as well.

3.1.2.1 Availability of Toxicity Information

The extent of information on the toxicities associated with the potential TPH substitutes (the BTEX compounds, naphthalene, PAHs, and alkanes) varies with the compound. Of the BTEX compounds, benzene has been studied most extensively. Toxicities associated with ethylbenzene, toluene, and xylene could be located, and critical studies have been identified and peer reviewed by the USEPA. Similarly, naphthalene has well-defined toxicity; the USEPA continues to critically review napthalene toxicity papers. For the PAHs, the most extensively studied PAH is the higher molecular-weight benzo(*a*)pyrene (or B(*a*)P). This compound has been critically reviewed for its toxic effects, and the trend within the Agency has been to use this PAH as a measuring stick for assessing relative toxicities of other PAHs. The cyclic and straight chain alkanes have less toxicity information available, and do not typically have identified or peer reviewed critical studies. The general nature of the critical toxicities associated with the potential substitutes is discussed in the next section.

3.1.2.2 Toxic Effects

The toxic effects associated with chronic exposures (long term or lifetime) to potential substitutes are considered for these analyses, as being most representative of exposures associated with land use at spill sites, and being more conservative (*i.e.*, more protective) of human health.

The relative toxicities of the BTEX compounds, naphthalenes, PAHs, and alkanes can be categorized according to their carcinogenic and noncarcinogenic potential. Of the BTEX compounds, benzene has been classified as a human carcinogen. The PAH, B(*a*)P, has been classified as a probable human carcinogen. Certain other higher molecular-weight PAHs have also been classified as probable carcinogens, in addition to having noncarcinogenic toxic effects. The remainder of the BTEX compounds (*i.e.*, the alkylbenzenes toluene, ethylbenzene, and the xylenes), as well as naphthalene, exhibit only noncarcinogenic effects of varying severity. Normal and cyclic alkanes are not typically considered to cause significant adverse health effects, particularly for chronic exposures.

For purposes of these analyses, compounds exhibiting carcinogenic endpoints are viewed as being more prone to be risk drivers, from human health and a regulatory perspectives. However, for compounds with carcinogenic and noncarcinogenic potential (benzene and B(*a*)P), both toxicities are considered, where possible.

3.1.2.3 Availability of Benchmark Toxicity Values

As mentioned above, for purposes of this selection process, the most significant adverse effects (*e.g.*, carcinogenicity) were considered to be those exhibited from chronic exposures, followed by chronic noncarcinogenic effects. Most of the potential substitutes have toxicity values that have been established and peer reviewed by the USEPA (USEPA 1992, 1993). Potential substitutes with established toxicity values are shown in **Table 3-5** (BTEX) and **Table 3-6** (nonBTEX, potential TPH substitutes). A tentative approach for deriving carcinogenic toxicity values for several of the high molecular-weight PAHs (probable human carcinogens) has been proposed by the USEPA ("relative potency estimates", Schoeny 1993), although it is currently undergoing technical and policy reviews. The application and implications of these toxicity values will be discussed in subsequent sections.

3.1.3 Availability of Regulatory Standards for Relevant Media

Based on current state and federal trends in regulating BTEX and TPH concentrations in soil, the potential migration of contaminants to ground water is of primary concern for both present and future land use. The approach to determining the maximum soil concentration that corresponds to associated unacceptable ground water concentrations typically involves identification or establishment of health-based ground water concentrations, either federal or state-specific, and then modeling soil concentrations that will not cause an exceedance of the ground water standards. To varying degrees of scientific rigor and extent, existing or emerging models are being used to derive soil concentrations that maintain ground water concentrations within federal or state standards. In some cases, site-specific contingencies are built into the "allowable" soil levels to accommodate site-specific conditions, such as potability of the ground water, distances to well heads, soil type, and soil permeability.[8] Policies for establishing soil cleanup concentrations that allow for the use of site-specific parameters have greater flexibility than those which attempt to establish a generic soil cleanup concentration applicable to all sites. The nonhomogeneous nature of regional geological and hydrogeological properties at the sites of JP-4 spills often makes it impossible to apply a generic dilution factor or a chemical-specific mobility retardation factor. Soil compositions vary greatly, subsurface soil strata are nonhomogeneous, depths to ground water vary, precipitation rates can differ greatly, interactions between ground water and surface water can be complex and the actual nature of the ground water aquifers in question is bound to differ, even on a subregional scale. Ideally, all of these factors could be accounted for and their relative contributions factored into the estimation of the soil-ground water dynamics. Therefore, while attenuation factors can be applied to the transport of contaminants through the soil column, their generic application to every site under consideration can yield erroneous soil cleanup concentrations.

Establishing soil cleanup concentrations corresponding to *acceptable risks* adds a new level of complexity. In determining remediation goals protective of human health, risks associated with both ingestion of soil and ingestion of underlying ground water must be determined. Certainly, the potential for future contamination of any underlying ground water that may serve as a drinking water source should also be considered. The acceptable ground water concentrations for contaminants in drinking water sources are governed by the federally established National Primary Drinking Water Standards (NPDWS), which exist as enforceable standards termed Maximum Contaminant Levels (MCLs). Cleanup efforts for soils would have to ensure that future ground water concentrations not exceed any MCLs for the potential TPH substitutes. The available MCLs for all potential substitutes are listed in **Table 3-7**.

3.2 Application of Selection Criteria to Potential TPH Substitutes

Preliminary selection of potential TPH substitutes identified the following JP-4 constituents:

- BTEX compounds (*i.e.*, benzene, toluene, ethylbenzene, xylene);
- Polyaromatic hydrocarbons (select PAHs);
- Naphthalene(s); and,
- Normal alkanes (*e.g.*, hexanes, octanes) and cycloalkanes (*e.g.*, cyclohexane).

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[8] For example, Alaska, Idaho and Washington have developed matrices which allow for the adjustment of soil TPH/BTEX cleanup levels based on site specific-features including: depth to subsurface water, annual precipitation, volume of contaminated soil, and soil or rock type.

A substitute-specific analysis of the fate and transport properties and toxicological effects of these compounds that will influence the selection of the TPH substitute of choice is presented in the following sections.

3.2.1 TPH

There are two predominant factors that limit consideration of TPH characteristics:

(1) product-specific variation, and
(2) analytical method-specific variation.

The constituents and relative proportions of potential chemicals of concern can be expected to vary greatly with the type of fuel or petroleum product. In addition, the method of analysis and quantification of TPH in a given medium will greatly affect the types and proportions of constituents that ultimately become classed as "TPH". These complications stem from the fact that TPH represents a highly complex mixture of chemicals, extracted from an even more complex original mixture. The all-inclusive aspect implied by use of the acronym TPH ("Total" Petroleum Hydrocarbons) is itself misleading for this very reason.

3.2.1.1 Fate and Transport

There are not likely to be TPH-specific fate and transport information that can consistently reflect the same contaminants, for a given medium, over time. While migration of certain constituents is bound to be influenced by the initial properties of the original petroleum product or fuel, over the course of weathering at the site, specific types of constituents should undergo transport in chemical- and site-specific manners. Measurements quantifying TPH over time, even within the same medium and location, will be indicators of a dynamically changing profile of constituents, with minimal intersample consistency. While temporal predictions could be made for the anticipated components of TPH in, for example, a surface soil sample, the lack of consistency in sample components over time would offer little useful information unless fairly extensive characterizations of the TPH constituent profile were made.

Qualitatively, it could be assumed that, for a very recent JP-4 spill, TPH in soils would reflect predominantly all constituents, with eventual loss of BTEX components first, lighter alkanes second, lighter PAHs third, followed by naphthalenes. For an aged spill, TPH might reflect predominantly trace amounts of high molecular-weight PAHs (*i.e.*, B(*a*)P). However, since these PAHs are not typically present in JP-4 fuel, it is more likely that the residuals would be higher molecular-weight and branched alkanes.

3.2.1.2 Toxicity

It is not anticipated that there would be any TPH-specific toxicity information, for the same reasoning applied to the fate and transport considerations. Measurements of TPH would be internally inconsistent over time with respect to the chemical components present. Given that the actual components of TPH will be highly site-specific, and analytical method-specific, the associated toxicity will vary as well. If the qualitative fate and transport considerations are applied, then the toxicity of TPH should vary over time based on the presence of the anticipated constituents.

There are no established or proposed TPH-specific toxicity values.

3.2.2 Examination of BTEX

Fate and transport parameters for the BTEX compounds, as well as the critical, predominant toxicities associated with these compounds are presented in the following two sections.

3.2.2.1 Fate and Transport

Based on their relatively high vapor pressures and moderate to high water solubilities, the BTEX compounds typically exhibit high mobility in soils. They volatilize extensively to air following a surface spill, and from surface water following a spill and subsequent transport processes. The relatively low Koc's indicate nonextensive to moderate association with organic carbon in soils, especially in light of their water solubilities. Trends towards decreased leaching (effectively, soil migration) with increasing soil organic carbon fraction have been observed for toluene and the xylenes. All BTEX compounds undergo biodegradation in soil or water, although benzene biodegradation in soil is minimal. The nature and extent of biodegradation appears to be highly influenced by the degree of oxygenation of the soils, as well as other site-specific parameters. BTEX compounds have been found in association with ground water, although toluene is not typically encountered to any significant extent.(ATSDR 1990a, 1990c, 1992b, 1993).

3.2.2.2 Toxicity

The chronic toxicities of the individual BTEX compounds are driven primarily by the toxic properties of benzene. Benzene is a known carcinogen in animals and humans, both orally and via inhalation. Increased risk of leukemia in occupationally exposed persons (Ott *et al.* 1978; Rinsky *et al.* 1981; Rinsky *et al.* 1987, Wong *et al.* 1983) and in animal studies (Cronkite *et al.* 1984, 1986, 1989; Maltoni *et al.* 1982) supports this conclusion . In addition, benzene has been shown to be harmful to the immune and hematopoietic systems (Snyder *et al.* 1980; Rozen and Snyder 1985; ATSDR 1992b). Ethylbenzene, toluene, and xylenes exhibit similar types of acute toxic effects, primarily manifested as depression of the central nervous system (CNS) and respiratory impairment, with reported effects on the liver, kidneys, and hematopoietic system (ATSDR 1990a, 1990c, 1993). Some evidence of teratogenicity (adverse effects on fetuses) have been reported for xylenes (ATSDR 1990c) and ethylbenzene (Andrew *et al.* 1981; ATSDR 1990a) although there are complications in interpreting these studies.

The established benchmark toxicity concentrations for these compounds are shown in **Table 3-5**.

3.2.3 Examination of Other Potential TPH Substitutes

Potential TPH substitutes, in addition to the BTEX compounds, are discussed below, with respect to their specific fate and transport characteristics and their respective critical toxic effects.

3.2.3.1 Alkanes

The lower molecular-weight alkanes, such as hexane, heptane, and cyclohexane, are discussed in this section. There is a paucity of information on higher molecular-weight alkanes.

3.2.3.1.1 Fate and Transport

The physicochemical properties of the alkanes such as hexane, heptane, and cyclohexane indicate that they are fairly volatile compounds, and therefore will tend to vaporize following spills. However, unlike the BTEX compounds, their hydrophobic nature, and affinity for organic carbon does not indicate a great tendency to leach and migrate into subsurface soils or ground water (CRC 1986).

3.2.3.1.2 Toxicity

Alkanes such as hexane, heptane, octane, and cyclohexane exhibit related toxicity following acute exposure, such as CNS depression at fairly high levels. *n*-Hexane chronic toxicity includes peripheral nerve damage in workers exposed by inhalation (Iida and Yamamoto 1973; ACGIH 1990) and animals (Spencer 1980; ACGIH 1990a). Minimal negative evidence for heptane chronic toxicity was found (API 1980; Crespi *et al.* 1979). No information was found on octane toxicity in humans or animals. Chronic to subchronic cyclohexane exposures in animals indicate minimal-to-no observations of neural and other tissue toxicity (ACGIH 1990b; Patty 1981-2; Frontali *et al.* 1981) although it has been suggested that cyclohexane may function as a weak tumor promotor (Gupta and Mehrotra 1990). Additional information for these compounds is limited, as they have not been associated with particularly toxic endpoints.

There are no established toxicity values for these compounds.

3.2.3.2 Naphthalene

Naphthalene is a relatively low molecular weight, aromatic compound comprised of two fused rings.

3.2.3.2.1 Fate and Transport

Naphthalene is moderately volatile, and has a fairly low water solubility, a relatively high K_{ow}, and a moderate affinity for organic carbon. These characteristics do not indicate a great tendency to migrate into subsurface soil or ground water. Biodegradation has been noted for soil and water, although the nature and extent of these processes are site-specific (ATSDR 1990d).

3.2.3.2.2 Toxicity

Naphthalene carcinogenicity in animals has been studied by the National Toxicology Program (NTP 1991) and Adkins *et al.* (1986), with equivocal outcomes on carcinogenicity although it has caused hemolytic anemia following both chronic and acute exposures. Both the liver and the hematopoietic system have been indicated as sites of naphthalene toxicity (ATSDR 1990d).

The existing benchmark toxicity concentrations for naphthalene are shown in **Table 3-6**.

3.2.3.3 PAHs

The PAHs typically include those organic compounds with three or more fused aromatic rings in their structures. The vast majority of the high molecular-weight PAHs are not associated with JP-4 fuel. However, those PAHs that are associated with JP-4 fuel represent some of the fuel's heavier compounds.

3.2.3.3.2 Fate and Transport

Polyaromatic hydrocarbons are a broad class of compounds with respect to their molecular weights and properties. In general, lower molecular-weight PAHs (*e.g.*, fluorene) are more water soluble and exhibit greater soil mobility than higher molecular-weight PAHs. However, as a chemical group, these compounds are not considered particularly volatile or mobile in terms of their environmental fate and transport. Therefore, PAHs tend to remain associated with soils, rather than leaching into ground water. The higher molecular-weight PAHs have much less potential for migration into ground water. While the primary fate of these compounds in soils is biodegradation, the actual extent of biodegradation and reduction of soil levels cannot be established as a fixed variable, since site-specific microorganisms and spill conditions are the driving factors in the process.

3.2.3.3.1 Toxicity

The predominant toxicity associated with PAHs (primarily select high molecular-weight PAHs) is carcinogenicity. However, the PAHs that are classed by the USEPA as probable human carcinogens (*e.g.*, benzo(*a*)pyrene, benz(*a*)anthracene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, chrysene, and, dibenz(*ah*)anthracene) have not been detected in appreciable amounts in jet fuels, with the exception of chrysene (USEPA 1980; chrysene present at less than 4 ppb).[9] The carcinogenic effects have been best defined for the PAH benzo(*a*)pyrene, a potent skin and lung carcinogen in animals. In addition, it has been demonstrated that benzo(a)pyrene (B(a)P) is a cause of adverse reproductive effects and is teratogenic (ATSDR 1990b). Noncarcinogenic PAHs that have been detected in jet fuels include phenanthrene, anthracene, fluoranthene, pyrene, benzo(*e*)pyrene, and fluorene, which exhibit variable to unknown degrees of toxicity.

As part of their efforts to develop PAH-specific carcinogenic toxicity values, the USEPA's proposed approach of "relative potency factors" was developed (USEPA 1993b). Past attempts to derive toxicity equivalency factors for PAHs based on their carcinogenicity relative to benzo(*a*)pyrene (ICF-Clement 1988) posed inherent problems. A more recent approach tentatively proposed by the USEPA (the Relative Potency Estimate approach, USEPA 1993b) is similar, and provides a means for deriving relative cancer slope factors for six other high molecular-weight carcinogenic PAHs (benz(*a*)anthracene, benz(*b*)fluoranthene, benz(*k*)fluoranthene, chrysene, dibenz(*ah*)anthracene, and indeno(1,2,3-*cd*)pyrene). With the exception of chrysene, these PAHs are not constituents of jet fuels (USEPA 1980). This approach cannot be applied to the PAHs in jet fuel most likely to migrate from soil to ground water, like fluorene, since these jet fuel PAHs are not carcinogenic. However, this approach could be applied to chrysene, a higher molecular-weight PAH in jet fuel that tends to remain associated with soils, since chrysene is a carcinogen. The basic approach compares the magnitude of the carcinogenic properties of six PAH carcinogens to that of B(*a*)P and normalizes them to B(*a*)P. A PAH-specific adjustment factor (an *order-of-magnitude* factor) is then applied to either known soil concentrations of these PAHs or to the B(*a*)P slope factor, to essentially express PAH-specific carcinogenicity in what equates to B(*a*)P equivalents. The order-of-magnitude adjustment factor for chrysene, the sole carcinogenic PAH present in trace amounts in jet fuels, is 0.01 (USEPA 1993b). When this adjustment factor is applied to the B(*a*)P oral slope factor of 7.3 (mg/kg/day)$^{-1}$ (USEPA 1993a), an oral slope factor of 0.073 (mg/kg/day)$^{-1}$ can be ascribed to chrysene. This toxicity value is shown in **Table 3-6.**

3.2.4 Summary

Substitute-specific fate and transport properties. In a new JP-4 spill, BTEX and lower molecular-weight alkane substitutes (*e.g.*, hexane, octane, and cyclohexane) are the volatile

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[9] The order of potencies for seven PAHs has been estimated as follows (USEPA 1993b): dibenz(a,h)anthracene > benzo(a)pyrene > benzo(b)fluoranthene > benz(a)anthracene >_ indeno(1,2,3-cd)pyrene > benzo(k)fluoranthene > chrysene

constituents (ATSDR 1992a). Given their lower molecular-weights, relatively higher water solubilities, and greater soil mobilities, these constituents tend to leach into soil with surface water precipitation and migrate over greater vertical distances than the other potential substitutes.

The primary fate of PAHs that do not volatilize and tend to remain associated with soils, appears to be biodegradation (ATSDR 1990b, 1992a), although the nature and extent of this activity will vary widely with such factors as the size of the spill, the soil type, and soil microbial characteristics. Transport (*e.g.*, percolation or leaching) of higher molecular-weight PAHs associated with jet fuels (*e.g.*, benzo(*e*)pyrene, chrysene, and fluoranthene) is limited by their soil affinity and low water solubility. These compounds are hydrophobic in nature and tend to remain associated with the organic carbon fraction in soil, as opposed to the percolating water phase. Lower molecular-weight PAHs, such as fluorene, have been shown to exhibit faster migration rates than their higher molecular-weight counterparts (ATSDR 1990b, 1992a) and are most likely to reach the water table.

Naphthalene and substituted naphthalenes, by virtue of their smaller size and greater relative water solubility, are also expected to be transported further, although perhaps not as rapidly as the BTEX and alkanes.

Therefore, higher molecular-weight PAHs and possibly some naphthalene would appear to remain associated with the soils at the site of the spill for significantly longer periods of time than BTEX, while BTEX, naphthalene, and low molecular-weight PAHs would be anticipated to migrate further, thereby exhibiting a greater potential for ground water contamination.

Substitute-specific toxicity and established benchmark toxicity concentrations. A comparison of the magnitude of the toxicity values for the carcinogenic JP-4 constituents (oral slope factors for benzene and chrysene, **Tables 3-5 and 3-6**) indicates that the marginally larger slope factor is associated with chrysene (0.073 $(mg/kg/day)^{-1}$ for chrysene; 0.029 $(mg/kg/day)^{-1}$ for benzene). However, at this time benzene is still the only potential TPH substitute with an oral slope factor established by the USEPA's Carcinogen Risk Assessment Verification Endeavor (CRAVE). In addition, since the concentration of chrysene in JP-4 fuel tends to be much lower than that of benzene, benzene is more likely to exhibit a greater potential for ground water contamination than chrysene.

Comparisons of the noncarcinogenic toxicity values for potential TPH substitutes (**Tables 3-5 and 3-6**) indicate that the lowest chronic oral R_fDs and, hence, the greatest potential for producing adverse health effects under similar exposure conditions, are for naphthalene and several of the PAHs.

Table 3-1. Concentrations of BTEX Compounds in Fuels Similar to JP-4

Compound	Kerosene (ppm; mg/L)[a]	Jet A Fuel (ppm) [b]
Benzene	<1681	2521
Toluene	2773	11765
Ethylbenzene	3109	2521
Xylenes (total *o-,m-,p-*)	8067	7563

(a) In: ***Development of a Standard Pure-Compound Base Gasoline Mixture for Use as a Reference in Field and Laboratory Experiments.*** 1990. Kreamer and Stetzenbach. Values were converted from a range of weight percents to ppm (mg/L) by using the midpoint value of the weight percent range in combination with the midpoint value for the density of kerosene.
[weight percent (g/kg) × 1 kg kerosene/1.19 L × 1000 = ppm]

(b) In: *Soluble Hydrocarbons Analysis From Kerosene/Diesel Type Hydrocarbons.* Dunlap and Beckmann. Values were converted from weight percents in manner analogous to that described in footnote (a).

Table 3-2. Concentrations of Potential Substitutes in Fuels Similar to JP-4

Compound	Jet A Fuel (low sulfur) (ppb) (a)	Jet A Fuel (high sulfur) (ppb) (a)	Jet fuel (ppb) (b)	Fuel oil no. 1 (Kerosene) (ppm) (c)
Polyaromatic hydrocarbons (PAHs):				
Phenanthrene	1800	2200		210
Anthracene	140	200		0.84
Fluoranthene	12	48		
Pyrene	18	76		
Triphenylene	3.6	7.2		
Chrysene	2.8	3.2		
Benzo(*e*)pyrene	1.6	11.4		
Benzo(*a*)-anthracene	ND	ND		
Benzo(*a*)pyrene	ND	ND		
Benzo(*g,h,i*)-perylene	ND	ND		
Anthanthrene	ND	ND		
Corenene	ND	ND		
Flourene	ND	ND		
Total PAHs	1978	2546	150	151
Naphthalene	5882 ppm (d)			3781
Total Naphthalenes				
Alkanes:	NR	NR	NR	NR
n-Hexane				
Cyclohexane				
Total Alkanes				
Total Cycloalkanes				

(a) In: *Quantitative Analysis of Polynuclear Aromatic Hydrocarbons in Liquid Fuels*. 1980. USEPA, Environmental Sciences Research Laboratory, Reserach Triangle Park, NC. EPA-600/2-80-069. Values represent the average concentration for two samples.

(b) In: *Soil Cleanup Criteria For Selected Petroleum Products*. 1986. Stokman and Dime.

(c) In: *Development of a Standard Pure-Compound Base Gasoline Mixture for Use as a Reference in Field and Laboratory Experiments*. 1990. Kreamer and Stetzenbach. Values were converted from a range of weight percents to ppm (mg/L) by using the midpoint value of the weight percent range in combination with the midpoint value for the density of kerosene. [weight percent (g/kg) x 1 kg kerosene/1.19 L x 1000 = ppm]

(d) In: *Soluble Hydrocarbons Analysis From Kerosene/Diesel Type Hydrocarbons*. Dunlap and Beckmann. Values were converted from weight percents in manner analogous to that described in footnote (b).

NR = Not Reported

Table 3-3. Physical-Chemical Properties of Potential TPH Substitutes

Chemical	Molecular Weight	Boiling Point (°C)	Vapor Pressure (mm Hg)	Henry's Law Constant (atm-m^3/mole)	Water Solubility (mg/L)	Organic Carbon Partition Coefficient (K_{oc})	Octanol Water Partition Coefficient (K_{ow})
Range of Values (Bold values indicate higher soil mobility)	**78.1** to 252.3	**69** to 448	5.6×10^{-9} to **400**	4.9×10^{-7} to **3.21**	3.8×10^{-9} to **1780**	**48** to 5.5×10^6	**135** to 1.55×10^6
BTEX							
Benzene[a]	78.1	80.1	95	5.5×10^{-3}	1780	63-79.4	135
Ethylbenzene[b]	106	136.3	9.5	8.7×10^{-3}	160-208	165-254	1349-2200
Toluene[c]	92.1	110.6	22	6.7×10^{-3}	448	295	617
Xylenes[d] (*o*-,*m*-,*p*-)	106.2	137-144	6.7-10	$5.2\text{-}7.6 \times 10^{-3}$	134-213	48-260	1202-1585
Potential Surrogates							
Alkanes:							
Heptane[e]	100.2	98.4	~40	2.06	2.4	2400-8100	$10^{4.66}$
Hexane[e]	86.2	69	$100 < x < 400$	1.81	9.5	1250-4100	$10^{3.9}\text{-}10^{4.11}$
Octane[e]	114.2	125.7	~10	3.21	7×10^{-4}	5500-15,600	$10^{4}\text{-}10^{5.18}$
Cycloalkanes:							
Cyclohexane[e]	84.2	80.7	100	0.19	54.8	480	No data
Naphthalene[f]	128.2	218	0.087	4.6×10^{-4}	31.7	933	1950

Table 3-3. Physical-Chemical Properties of Potential TPH Substitutes (continued)

Chemical	Molecular Weight	Boiling Point (°C)	Vapor Pressure (mm Hg)	Henry's Law Constant (atm-m^3/mole)	Water Solubility (mg/L)	Organic Carbon Partition Coefficient (K_{oc})	Octanol Water Partition Coefficient (K_{ow})
PAHs:							
Anthracene(g)	178.2	340-342	1.7×10^{-5}	8.6×10^{-5}	No Data	1.4×10^{4}	2.8×10^{4}
Benzo(*a*)-pyrene(g)	252.3	310-312	5.6×10^{-9}	4.9×10^{-7}	3.8×10^{-9}	5.5×10^{6}	1.55×10^{6}
Chrysene(g)	228.3	448	6.3×10^{-9}	1.0×10^{-6}	1.5×10^{-3}	2.0×10^{5}	4.1×10^{5}
Flouranthene(g)	202.3	375	5.0×10^{-6}	6.5×10^{-6}	No Data	3.8×10^{4}	7.9×10^{4}
Flourene(g)	166.2	295	7.1×10^{-4}	6.4×10^{-5}	1.7-2.0	7.3×10^{3}	1.5×10^{4}
Pyrene(g)	202.3	393-404	2.5×10^{-6}	5.1×10^{-6}	0.13-0.17	3.8×10^{4}	8.0×10^{4}

(a) Toxicological Profile for Benzene. ATSDR. 1992b.
(b) Toxicological Profile for Ethylbenzene. ATSDR. 1990a.
(c) Toxicological Profile for Toluene. ATSDR. 1993.
(d) Toxicological Profile for Total Xylenes. ATSDR. 1990c.
(e) CRC Handbook of Chemistry and Physics. 67th ed. 1986-87.
(f) Toxicological Profile for Naphthalene, 2-Methylnaphthalene. ATSDR. 1990d.
(g) Toxicological Profile for Polyaromatic Hydrocarbons. ATSDR. 1990b.

Table 3-4. Anticipated Temporal Variations in Relative Proportions of BTEX and High MWr PAH Substitutes

Relative Age of Spill	BTEX	PAHs
Recent, fresh spill	Surface Soil: High levels Groundwater: None	Surface Soil: High levels Groundwater: None
Older spill	Surface Soil: Low levels Groundwater: Low levels; typically benzene	Surface Soil: High to moderate Groundwater: None to traces of low MWr PAHs; *e.g.*, flourene
Old Spill	Surface Soil: None to trace Groundwater: Low levels; BTEX	Surface Soil: Moderate levels of high MWr PAHs; *e.g.*, B(a)P Groundwater: Trace to low levels of low MWr PAHs

Table 3-5. Toxicity Values For BTEX Compounds

Chemical	Chronic Oral R_fD (mg/kg/day)	Inhalation Reference Dose (mg/m^3)	Oral Slope Factor $(mg/kg/day)^{-1}$	Inhalation Unit Risk (Risk/(mg/m^3)
Carcinogens:				
Benzene	Not Available	Not Available	2.9×10^{-2}	8.3×10^{-6} per ($\mu g/m^3$) [unit risk]
Noncarcinogens:				
Toluene	2×10^{-1}	4×10^{-1}	Not Applicable	Not Applicable
Ethylbenzene	1×10^{-1}	1×10^{0}	Not Applicable	Not Applicable
Xylenes [*o*-,*m*-,*p*-]	2×10^{0}	Not Available	Not Applicable	Not Applicable

Table 3-6. Toxicity Values For Additional Potential TPH Substitutes

Chemical	Chronic Oral R_fD (mg/kg/day)	Inhalation Reference Dose (mg/m^3)	Oral Slope Factor $(mg/kg/day)^{-1}$	Inhalation Unit Risk ($Risk/(mg/m^3)$)
Polyaromatic Hydrocarbons:				
Anthracene	3×10^{-1}	---	Not Applicable[a]	Not Applicable
Benzo(*e*)-pyrene	---	---	Not Applicable[b]	Not Applicable
Chrysene	---	---	0.073[c]	Not Available
Fluoranthene	4×10^{-2}	---	Not Applicable[a]	Not Applicable
Fluorene	4×10^{-2}	---	Not Applicable[a]	Not Applicable
Phenanthrene	---	---	Not Applicable[a]	Not Applicable
Pyrene	3×10^{-2}	---	Not Applicable[a]	Not Applicable
Alkanes: Hexane, Octane, or Cyclohexane	None Available	None Available	Not Applicable	Not Applicable
Naphthalene	4×10^{-2}[d]	Not Available	Not Applicable	Not Applicable

(a) USEPA 1993. Integrated Risk Information System (IRIS), NLM on-line database was consulted.

(b) Benzo(a)pyrene has an oral slope factor of 7.3 $(mg/kg/day)^{-1}$, but benzo(e)pyrene is not currently considered a carcinogen.

(c) USEPA 1993b. Chrysene oral slope factor derived via "relative potency factor" approach. See text for detailed explanation.

(d) Naphthalene toxicity values are currently undergoing extensive review by the USEPA R_fD Work Group. These values are from the Health Effects Assessment Tables (HEAST) for 1991; as such, they are subject to potential alterations in the future.

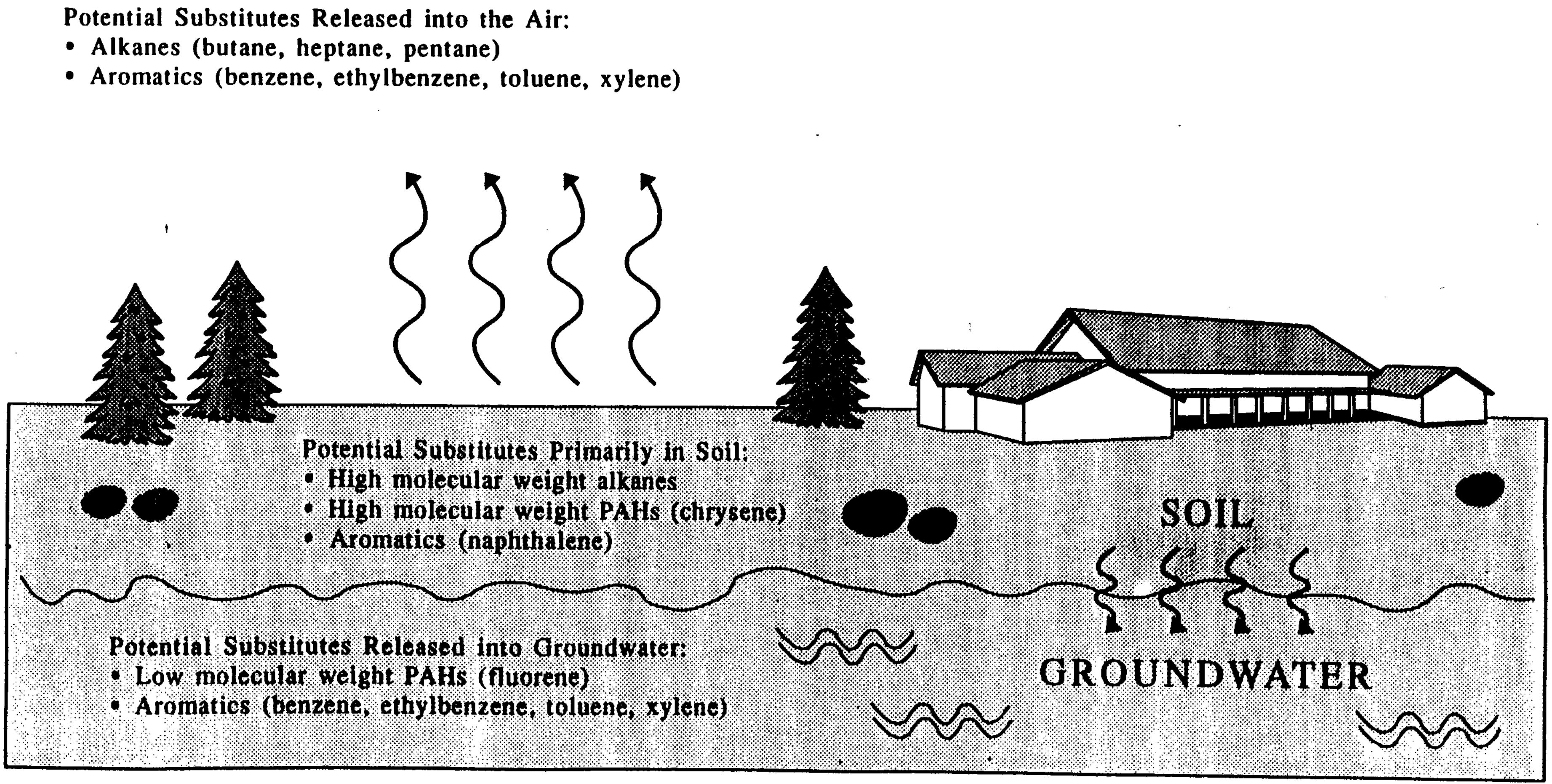
Table 3-7. Maximum Contaminant Levels (MCLs or NPDWRs) for BTEX and Potential TPH Substitutes

Chemical	MCL (ppm)(a)
Alkanes (cyclohexane, hexane, octane)	Not Listed
Benzene	0.005
Ethylbenzene	0.7
Naphthalene	Not Listed
PAHs: Benzo(*a*)pyrene(b) Other PAHs	 0.0002 None
Toluene	1.0
Xylene	10.0

(a) MCLs are taken from the Final and Proposed Drinking Water Standards (40 CFR 141), July 1992.

(b) Benzo(a)pyrene is not present in jet fuels. It is listed here because it is the only PAH with an MCL.

Figure 3-1. Fate and Transport of Potential TPH Substitutes



4.0 SELECTION OF THE APPROPRIATE TPH SUBSTITUTE(S)

Summary: ***Section 4.0*** *uses all of the information compiled and assessed in* ***Sections 2.0 and 3.0*** *to select the preferred TPH substitute. As explained in* ***Section 1.0****, the desire is to select a standard that is both scientifically defensible and based on human health risk, rather than on best available technology.* ***Section 4.0*** *describes the health risk assessment process and how it leads to the development of a preliminary remediation goal (PRG) for soil cleanup. Specific chemicals in the four chemical groups identified in* ***Section 3.0*** *(BTEX, naphthalenes, PAHs, and alkanes) were then considered in the context of human health risk and the development of a soil PRG. To do this, the following criteria were considered: toxicity, availability of toxicity benchmark values, the calculated PRGs, anticipated environmental fate and transport, potential for contaminating other environmental media, and relevance of state-specific approaches to regulating soil contaminants. Based on these criteria, benzene was selected as the preferred TPH substitute.*

The final selection of the appropriate TPH substitutes is made based on several considerations that will influence the magnitude of a health risk-based soil cleanup concentration. To this end, the current human health risk methodology is briefly discussed as it relates to the development of soil cleanup concentrations protective of human health for each potential substitute. The final selection of the substitute of choice is presented with additional supportive information.

4.1 Current Methodology for Establishing Health Risk-Based Soil Cleanup Concentrations

The human health risk assessment process and the potential to establish health risk-based cleanup concentrations for chemicals of concern in discrete media are discussed in the following sections.

4.1.1 The Human Health Risk Assessment Process

The USEPA approach to human health risk assessment for chemicals essentially follows the approach first articulated by the U.S. National Academy of Sciences (NRC 1983). The four elements of risk assessment include:

- **Hazard Identification** - establishes the relationship between exposure to a chemical and a specific adverse health effect. Chemicals of potential concern for all given media are identified, and their hazardous properties are defined.
- **Dose-Response Assessment** - describes the quantitative relationship between the amount of a chemical to which individuals come into contact, and the degree and severity of known toxic injury or disease. The outcome of the dose-response

assessment is a benchmark concentration that expresses a threshold, with a margin of safety, above which toxic injury or disease may occur. A compound-specific reference dose, R_fD, is the toxicity value generally used in evaluating the noncarcinogenic effects of substances. To evaluate the potential risk of carcinogens, USEPA uses a two-part evaluation in which the substance first is assigned a weight-of-evidence classification that describes the likelihood that the agent is a human carcinogen; and secondly, a toxicity value is calculated that defines quantitatively the relationship between dose and response (*i.e.*, the slope factor, SF).

- **Exposure Assessment** - describes the human population exposed to chemical agents, and the quantity and duration of individuals' exposures. Typically, land use, human receptors of potential concern, and exposure pathways and specific routes are identified. The final outcomes of the exposure assessment are chemical-specific estimates of chemical intakes associated with the exposure pathways for those receptor populations that could potentially be exposed.

- **Risk Characterization** - integrates the data and analyses from the first three steps of risk assessment. It is used to determine the likelihood that some members of the population of interest may experience any of the various forms of toxicity associated with a chemical under the existing conditions of exposure. In this step, the noncarcinogenic and carcinogenic toxicity benchmark values (*i.e.*, R_fDs and SFs, respectively) for the chemicals of concern are used in conjunction with the estimated chemical intakes for the modeled populations to quantitatively estimate carcinogenic and noncarcinogenic risk.

The risk assessment process has been described in a systematic method; USEPA guidance documents provide methods for organizing, analyzing, and presenting information on the nature and magnitude of risks to public health from potential exposure to chemicals (*e.g.*, USEPA 1989).

Standard equations and exposure parameters exist to ascertain the Lifetime Average Daily Intake (LADI) from ingesting a compound in soil (USEPA 1989). The LADI can then be used to calculate risk (USEPA 1989):

$$\textit{Cancer risk}_{\textit{ingestion}} = \textit{LADI x Oral Slope Factor} \tag{1}$$

$$\textit{Hazard Quotient}_{\textit{ingestion}}\ (HQ_i)\ \textit{for Noncarcinogenic Effects} = \frac{LADI}{R_fD} \tag{2}$$

According to the National Oil and Hazardous Substances Contingency Plan (NCP) (40 CFR Part 300), carcinogenic risk greater than 1×10^{-6} is generally regarded to be unacceptable. In the context of hazardous waste cleanup, site-specific cancer risk between 1×10^{-4} and 1×10^{-6} may be deemed acceptable by the appropriate regulatory authority, depending on site-specific conditions and variables. Noncarcinogenic effects are generally considered to be unacceptable when the HQ exceeds a value of one (1.0). Based on the two equations above, carcinogenic risk will increase with increasing oral SF and LADI (soil concentration-dependent). The HQ increases as the oral R_fD decreases and the LADI increases.

The potential for an unacceptable cancer risk or adverse noncancer health effect is a function of chemical potency and concentration in the soil. It follows that a "threshold" soil concentration can be back-calculated from the "threshold" risk that is acceptable.

A complementary outgrowth of the risk assessment process has been the formulation of methodologies for determining the chemical concentrations corresponding to the upper limits for acceptable carcinogenic or noncarcinogenic "risks" in various media of concern. The USEPA has established a set of guidelines for this risk-based approach to formulating what they term *Preliminary Remediation Goals*, or PRGs (USEPA 1991a). The use of the human health risk assessment process in formulating PRGs, as well as the implications and assumptions inherent in this process, are discussed in the following section.

4.1.2 Preliminary Remediation Goals (PRGs)

PRGs are designed to assist in the analysis and selection of remedial alternatives. They should be in compliance with any ARARs (applicable or relevant and appropriate requirements) and result in acceptable health risks for the given medium at the site. Chemical-specific PRGs are the concentrations of the chemical for a given medium and land use combination. Therefore, two general sources of PRGs are: (1) concentrations based on ARARs; and (2) concentrations based on health risk assessment. ARARs that must be met include those for the medium as well as other media that could be impacted (*i.e.*, ground water). Risk-based calculations that set medium-specific concentration limits, using carcinogenic and/or noncarcinogenic toxicity benchmark values in conjunction with exposure assumptions, must satisfy the NCP (40 CFR Part 300) requirements for protection of human health.

The typical approach advocated by the USEPA in establishing PRGs is to identify PRGs at the site-scoping stage, modify them during and after the Remedial Investigation (RI) using site-specific information, and ultimately select site remediation levels in the Record of Decision (ROD). In the context of this report, this might initially involve identification of soil ARARs for potential chemicals of concern (*e.g.*, TPH, BTEX, other TPH substitutes) and development of PRGs for nonARAR chemicals of concern (*e.g.*, BTEX, or others). In general, chemical-specific soil ARARs may not be available, although this report has identified state-specific soil cleanup concentrations for BTEX compounds with varying degrees of "enforceability", ranging from screening or action levels, to guidelines, to goals or actual standards.

USEPA PRGs are based on definition of the ***future*** land use of the site and, in the absence of definitive evidence for a particular scenario, residential land use is typically the land use of choice. According to USEPA PRG guidance, residential land use requires that PRGs be formulated for the soil ingestion route of exposure, where an individual has been living onsite from birth through 30 years of age. In this manner, human health risk calculations will encompass exposures for both a child and an adult — effectively the most conservative estimates of risk (*i.e.*, they will result in the lowest soil cleanup concentration, since exposure includes that of the most sensitive human receptor).

The approach for formulating a PRG for a single chemical in a single medium (*e.g.*, soil) is the derivation of the soil concentration that will yield either an "acceptable" carcinogenic risk level of 1×10^{-6} or an "acceptable" noncarcinogenic hazard quotient (HQ) of one (1.0), for the human receptor of primary concern. When the potential exists for risks to be generated from exposure to the same chemical in multiple media, an approach similar in rationale, yet slightly more complicated in application, is advocated. When risks to the human receptor of concern are associated with their concurrent exposure to more than one medium (*i.e.*, soil and air), and hence more than one route of exposure (*i.e.*, ingestion and inhalation), the risk is considered in an additive manner. For example, if an adult person ingests surficial soil from a given area on a site, while simultaneously inhaling volatile compounds emitted from the soil, the acceptable carcinogenic risk level for **both** exposure pathways would still be 1×10^{-6}, or the noncarcinogenic hazard quotient of 1.0 for both exposure pathways. The calculation of the corresponding acceptable soil concentration must now incorporate the exposure information for both routes of intake.

In summary, preliminary screening for assessing potential adverse health impacts attributable to the ingestion and/or inhalation of contaminated soils can be performed using either standard or refined risk-based PRG approaches. Standard equations and exposure parameters exist for ascertaining the soil PRG for either a noncarcinogenic or a carcinogenic compound obtained from ingestion of soil, or from ingestion of soil and inhalation of vapors and particulates (USEPA 1991a). In accordance with USEPA guidance, the land use for the site determines the routes of exposure that must be included in the PRG approach. Typically, for residential land use (either current or future), the route must involve soil ingestion for an adult who has been exposed since childhood for 30 years. For commercial/industrial land use, these routes must include soil ingestion, coupled with inhalation of soil vapor and soil particulates for an adult worker onsite. The approaches detailed in the USEPA guidance for PRGs were followed in the subsequent sections addressing the estimation of soil cleanup concentrations.

4.2 Soil Cleanup Concentrations for TPH Substitutes

As discussed in the previous sections, application of the PRG risk-based approach to formulating soil cleanup values was used to estimate relative soil cleanup concentrations for the potential TPH substitutes. These estimates were based on the assumption that exposure occurs primarily via ingestion of site soil under assumed future residential land use. The potential for estimating soil cleanup concentrations for soil ingestion and the inhalation exposure route is also discussed, along with its inherent limitations.

4.2.1 Soil Cleanup Concentrations Based on Soil Ingestion

Using the PRG health risk-based approach, soil cleanup concentrations can be formulated for all chemicals with established toxicity benchmark values, for both noncarcinogenic and carcinogenic effects. The equations and assumptions used to calculate the noncarcinogenic PRG for soil based on soil ingestion are shown in **Figure 4-1**. Similarly, equations and assumptions for estimating the carcinogenic PRG for soil based on soil ingestion are shown in **Figure 4-2**. The dependence of the noncarcinogenic and carcinogenic soil PRGs on either the noncarcinogenic R_fD or the carcinogenic SF are best illustrated in the reduced versions of each equation, shown at the bottom of each figure. The magnitude of the noncarcinogenic PRG is directly proportional to the established toxicity value (oral R_fD, R_fDo), while the carcinogenic PRG is inversely proportional to the magnitude of the carcinogenic toxicity value (oral SF, SFo). In other words, the greater the oral toxicity, either noncarcinogenic or carcinogenic, the lower the "acceptable" soil concentration.

The USEPA human health risk-based PRG approach has been applied to the estimation of soil cleanup concentrations for the potential TPH substitutes, using the PRG equations for the soil ingestion route of exposure. These cleanup concentrations are estimated primarily for purposes of comparison among the potential substitutes, as a preliminary indicator of the potential for each compound to drive a risk assessment or a remediation effort. Chemicals for which established toxicity values exist are included. Soil cleanup concentrations corresponding to "acceptable" risks are presented for both carcinogenic and noncarcinogenic toxic endpoints in **Table 4-1**. For carcinogenic and noncarcinogenic chemicals, the most conservative soil cleanup concentration is considered to drive the risk. The potential substitutes with the most conservative soil PRG estimates are chrysene and benzene, with PRGs of 8.8 ppm and 22 ppm, based on their carcinogenicity.

4.2.2 Soil Cleanup Concentrations for Soil Ingestion and Inhalation Exposure

For cases where compounds of concern may include volatiles, the inhalation pathway for vapors and soil particulates can be included along with soil ingestion in the estimation of the soil PRG. USEPA does not advocate this approach for residential land use, although for industrial land use, both of these pathways are considered for the onsite adult worker. It is not anticipated that risks associated with adult occupational exposure, even with the additional inhalation pathways, will exceed those risks calculated for the child/adult receptor under residential land use. The inclusion of exposure via vapor inhalation or inhalation of soil particulates requires knowledge of site-specific information on the nature and extent of the soil contamination with volatiles (*e.g.*, area of the spill or distribution of volatile samples, depth to encounter of volatiles, air temperature, and regional wind speed, among others). However, for demonstrative purposes, this report will consider a hypothetical commercial/industrial exposure which includes soil ingestion, as well as vapor and particulate inhalation routes, and presents information on both the modified risk-based equations and the limitations in making risk-based calculations in the absence of site-specific information.

Modified equations for potential use in estimating noncarcinogenic and carcinogenic soil PRGs, respectively, based on ingestion and inhalation exposure routes are shown in **Figures 4-3 and 4-4**. For each set of equations, the site-specific parameters required for deriving the soil PRG are indicated by bold, italicized text. The parameters requiring site-specific information were indicated in this manner to highlight the crucial role of site-specific input, which is especially relevant when considering the inhalation route of exposure. The lack of site-specific information essentially negates the quantification of a soil cleanup criterion for the hypothetical commercial/industrial land-use scenario. An examination of the simplified versions of these equations, shown on the bottom of each figure, indicates the direct dependence of the soil PRGs on the magnitude of the oral and inhalation R_fDs or the oral and inhalation SFs (*i.e.*, the greater the toxicity, the lower the PRG). The relationships between the PRGs and the site-specific parameters for the soil-to-air volatilization factor (VF) as well as on the particulate emission factor (PEF) are similar (the greater the volatilization and the emission from soil, the lower the soil PRG).

4.2.3 Soil Cleanup Concentrations for Inhalation Exposure Only

Because of the complexity of the issue, the ability to derive a soil cleanup concentration based solely on the inhalation exposure route will be demonstrated via illustration. Benzene is the only volatile compound which has an inhalation toxicity benchmark concentration. The unit cancer risk for benzene inhalation is 8.3×10^{-6} (corresponding to the risk associated with the inhalation of a unit dose of 1 $\mu g/m^3$ of benzene). A simple proportionality equation allows the determination of the air concentrations corresponding to an acceptable benzene risk level of 10^{-6} (since 1 $\mu g/m^3$ yields a risk of 8.3×10^{-6}, what benzene concentration yields a risk of 1×10^{-6}?) An inhalation risk level of 10^{-6} corresponds to an air concentration of 0.12 $\mu g/m^3$ of benzene, which can be converted to 0.037 ppb, using the benzene-specific conversion factor of 1 mg/m^3 = 0.31 ppm (ATSDR 1992b). This would be the air concentration associated with an "acceptable" risk level from benzene exposure (if exposure occurred for 24 hours/day for a lifetime of 70 years). This same value was calculated by the USEPA (1990) in *Leaking USTs and Health*. However, estimating the soil concentration corresponding to this "acceptable" air concentration could be modeled *only* for a site-specific exposure scenario, using site-specific input information (*e.g.*, a future exposure might be from emissions from an underground fuel spill into a residential basement).

4.2.4 Assumptions and Limitations

The estimation of soil cleanup concentrations based on the soil ingestion exposure pathway entails the use of several assumptions, and has limitations in usefulness, as well.

- The soil PRGs established in this report were estimated for the purposes of comparing their risk-based outcomes and determining which of the potential TPH substitutes were the predominant risk drivers.

- The actual soil cleanup concentrations generated using the PRG approach correspond to a residential future land use, and do not include the use of any exposure assumptions that are nonstandard from a risk assessment point of view (*i.e.*, all USEPA default values for exposure parameters were used, hence the PRG estimates are fairly conservative).

- The PRG approach has been established by the USEPA for application to CERCLA sites. As was discussed in **Section 2.1.1**, in the absence of USEPA-established soil cleanup concentrations for the BTEX compounds (or TPH), the primary regulatory agency with BTEX soil cleanup concentrations may be the particular state in which the site is located. Depending on the state-specific approach being used to estimate cleanup concentrations, the soil ingestion-based PRG may be a relevant consideration, but not necessarily the *final* consideration in setting a remediation standard in the Record of Decision.

- State-specific approaches for establishing soil cleanup concentrations for the BTEX compounds rely principally on human health protection, with the predominant trend toward the use of ground water standards. This approach is in variable stages of development and enforcement in many states; the use of somewhat more traditional health protective approaches, such as relying on soil ingestion as the primary exposure consideration, may receive variable weight in a risk management decision-making process.

4.3 Selection of Benzene as the TPH Substitute of Choice

Several factors must be considered in the final selection of the TPH substitute of choice, including toxicity, availability of an established toxicity benchmark concentration, the soil PRG, the anticipated fate and transport, the potential for contamination of other media, and the relevance to existing and emerging state-specific approaches to regulating soil contaminants. These points are considered in the following sections.

4.3.1 Relative Soil Cleanup Concentrations

When the relative toxicities of the potential TPH substitutes are considered, the compounds that have the most conservative toxicity concentrations are the carcinogens (**Tables 3-5 and 3-6**). The carcinogenic compounds, chrysene and benzene, are also those substitutes yielding the most conservative (*i.e.*, lowest) soil PRGs (**Table 4-1**). Substantially more toxicity information exists for benzene, and the carcinogenic endpoint has been studied extensively for multiple routes of exposure to benzene. Definitive carcinogenic toxicity benchmark values have been established for benzene (the oral SF and the inhalation unit risk). Chrysene, on the other hand, has substantially less supporting toxicity information. In addition, it has been assigned a relative potency factor as a means of *adjusting* its carcinogenicity relative to that of benzo(*a*)pyrene. To date there is no definitive oral SF for chrysene. In short, from the human health perspective, the overall weight-of-evidence for benzene carcinogenicity and the existence of recognized cancer slope factor information makes benzene a better candidate for a TPH substitute than chrysene.

4.3.2 Protection of Ground Water Standards

Consideration of the remaining factors, such as the anticipated fate and transport of benzene and chrysene, and the potential for contamination of other media, also point to benzene as the TPH substitute of choice.

The lower molecular weight of benzene, coupled with its higher water solubility and lower affinity for soils, indicates that benzene is more mobile than chrysene and will tend to percolate into soils to a greater and more rapid extent. Over time, chrysene can be expected to be more tightly associated with soil, and to leach more slowly. Based on these physicochemical properties, the potential for impacts to ground water, given similar site conditions, appears to be much greater for benzene. Therefore, there is greater potential for risks associated with the site to encompass multiple media and to be quantifiable therein.

The USEPA guidance for formulating PRGs also indicates the importance of considering the potential for cross-media contamination, via secondary sources. It suggests that for instances where the medium of concern (*i.e.*, soil) may appear to pose acceptable risk at a site, but where the medium may have the potential to contaminate another medium (*i.e.*, ground water), a new method for deriving a health-based PRG may need to be developed, provided that fate and transport information exists and can adequately predict potential impacts. As discussed in **Section 2.1.1**, the USEPA is currently developing a series of guidelines for BTEX compounds based on fate and transport modeling from soil to ground water. As was also discussed in **Section 2.1.1**, state-specific approaches to deriving soil cleanup concentrations have incorporated these methods as well, with variable levels of effort and results.

The approach to deriving the soil concentration corresponding to achieving the protective ground water concentration involves fate and transport modeling from soil to ground water. In some cases, such site-specific contingencies as:

- Ground water potability, under current or future land use;
- Distances to aquifers and well heads;
- Soil type; and,
- Soil permeability.

are built into the "allowable" soil concentrations to accommodate site-specific conditions. Soil cleanup policies that allow for site-specific considerations have greater flexibility than those based on a universal soil cleanup concentration or on a generic modeling approach to "reverse transport". While so-called soil retardation factors or attenuation factors can be applied to the transport of contaminants through the soil column, their universal application to every site under consideration would yield misrepresentative soil cleanup concentrations. Fate and transport modeling, provided site-specific information is incorporated, is a more reliable scientific tool.

Typically, the federal drinking water standards (Maximum Contaminant Levels (MCLs) or National Primary Drinking Water Regulations, (NPDWRs)), or state-specific drinking water or ground water quality criteria, are being used as the acceptable criteria for protecting drinking water sources. Chemical-specific MCLs are established to be protective of adverse human health effects for noncarcinogenic and carcinogenic effects for a lifetime via the oral drinking-water route of exposure. As such, the stringency of the MCL is driven by the stringency of the existing oral toxicities. All MCLs currently available for the potential TPH substitutes are listed in **Table 3-7**. Of the BTEX compounds, the MCL for benzene is lower (more stringent) than the MCLs for ethylbenzene, toluene, and xylenes by 140-, 200-, and 2000-fold factors, respectively. There are no MCLs for alkanes or PAHs associated with JP-4. There is no MCL for chrysene. The compound with the lowest MCL, and hence the most stringent ground water criterion, is benzene. A comparison of the relative potentials for migration to ground water of benzene and chrysene indicates that benzene, with its greater soil mobility, higher water solubility, and lower soil adsorption is the compound with the greatest potential to impact ground water.

4.3.3 Summary Information

There are insufficient bases for suggesting that any constituents of JP-4 other than benzene would serve as viable substitutes for TPH. This includes the three most promising candidate chemical groups--alkanes, naphthalene, and PAHs:

Alkanes. While alkanes are a primary component of JP-4 fuel, the spectrum of their toxicity, relative to the other potential candidates, does not represent the range of adverse toxicities exhibited by JP-4 or the known BTEX constituents. Also toxicity values and sufficient scientific information to support development of toxicity values have not been established. Alkanes are not considered to be carcinogenic compounds, and their primary acute noncarcinogenic effect (CNS depression) is not considered to have a significant potential for chronic adverse effects at anticipated chronic exposure levels. While these compounds are volatile and fairly mobile in soils (thereby increasing their potential to impact ground water via percolation, leaching, etc.), their potential for adverse toxic effects manifested through potential ingestion of ground water is not as significant as that of the other candidate substitutes or benzene.

Naphthalene. Naphthalene and substituted naphthalenes are present in lesser proportion than the alkanes in JP-4 fuel. However, naphthalene is a relatively low molecular-weight compound relatively mobile in soil and which has a fairly broad base of knowledge regarding its toxicity. The toxicity of naphthalene relative to the alkanes is more severe. The primary toxic effects are noncarcinogenic (*e.g.*, effects on the hematopoietic system, liver, and kidneys). Toxicity values for naphthalene are currently under review, although a federal drinking water standard does not exist for this compound in ground water. Relative to the toxicities of benzene and the higher molecular-weight PAHs, especially those exhibiting defined carcinogenic endpoints, naphthalene is not the best candidate to substitute for TPH.

Polyaromatic Hydrocarbons (PAHs), Chrysene. Polyaromatic hydrocarbons are a broad class of compounds with respect to their molecular weights and their toxic endpoints. In general, lower molecular-weight PAHs (*e.g.*, fluorene) are more water soluble and exhibit greater soil mobility than higher molecular-weight PAHs. However, as a chemical group, these compounds are not considered particularly volatile or mobile in terms of their environmental fate and transport. Therefore, they tend to remain more associated with soils rather than leach into ground water. In addition, the PAHs that are probable human carcinogens (*e.g.*, benzo(*a*)pyrene, benz(*a*)anthracene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, chrysene, and dibenz(ah)anthracene) have not been detected in jet fuels, with the exception of chrysene (USEPA 1980). These PAHs are higher molecular-weight compounds with much less potential for migration into ground water. While the primary fate of PAHs in soils is biodegradation, the actual extent to which this occurs to effectively reduce soil levels cannot be established as a fixed variable, since site-specific microorganisms and spill conditions are the driving factors in the process. The low tendency for these compounds to impact ground water and the lack of adequate scientific justification for apportioning relative risks among PAHs limit their usefulness as potential TPH substitutes in JP-4.

Conclusion. The physicochemical properties of benzene influencing its potential for ground water impact, the magnitude of and scientific understanding of its toxicity, and the availability of an established toxicity value, point to benzene as the substitute of choice for JP-4. Chrysene, the sole carcinogenic PAH in JP-4 considered as a possible substitute, is not as viable a substitute, given its less definitive toxicity benchmark value and lesser potential to impact ground water. Naphthalene is not a viable choice, given the lesser magnitude of the toxicity associated with naphthalene, the lack of an established toxicity benchmark concentration, and the lack of an MCL. Combined with the anticipated lack of carcinogenic PAHs in ground water, the lack of sufficient data regarding noncarcinogenic health effects, and the absence of MCLs for PAHs other than benzo(*a*)pyrene, *the TPH substitute of choice is benzene.*

4.4 The Potential for Simultaneous Achievement of Benzene and TPH Soil Cleanup Concentrations - A Comparative Approach

The degree of health and environmental protection that could be provided by the use of TPH cleanup concentrations at hydrocarbon-contaminated sites was compared to the degree of protection provided by cleanup of benzene to the PRG, resulting in a residual risk of less than 10^{-4} to 10^{-6}. A direct health risk-based comparison was not possible because of the inability to assess health risks for TPH and the lack of historical health risk-based approaches to establishing TPH cleanup concentrations. The following two hypothetical illustrations demonstrate this point.

4.4.1 Remediation to a Conservative TPH Soil Cleanup Concentration

Hypothesis 1: Cleaning up site soil to the conservative TPH method detection limit (10 ppm) will simultaneously achieve acceptable benzene risk levels. Because, in reality, site-specific scenarios are complex, simplifying points and assumption need to be stated:

- The estimated soil cleanup concentration for BTEX is driven by benzene;
- Soil ingestion is the principal exposure route of interest;
- A risk level of 10^{-6} is conservatively estimated to be achieved at a benzene soil concentration of 22 ppm (soil PRG);
- The lowest soil cleanup level proposed by a state for TPH is 10 ppm based on the current method detection level for TPH in soils; and,
- 100 percent of the TPH concentration is conservatively assumed to be benzene.

Based on these assumptions, a TPH-based soil cleanup level of 10 ppm will allow simultaneous achievement of the "acceptable" risk-based benzene soil cleanup concentration of 22 ppm.

Weaknesses in this illustration:

- It represents the soil medium and ingestion pathway only. Factoring the ground water medium (or air) or a ground water-protective cleanup strategy into the illustration will impact the ability of cleanup to TPH background to allow achievement of benzene cleanup concentrations, in a site-specific manner.
- The assumption that all TPH is benzene is purposely erroneous, since jet fuel typically contains less than 18 percent of total benzenes (benzene and substituted benzenes), and typically there is extensive volatilization of these compounds following a spill.

4.4.2 Remediation to a Benzene Soil Cleanup Concentration

Hypothesis 2: Cleaning up a site to a benzene 10^{-6} risk level (22 ppm) also achieves TPH cleanup to the method detection level (10 ppm). If BTEX was considered to be 100 percent benzene and was cleaned up to the 10^{-6} risk level of 22 ppm in soil, the TPH method detection limit may or may not be achieved. The major components of JP-4, the alkanes, may still be present in soil at a concentration greater than 10 ppm. If contamination occurred substantially in the past, it is more likely that cleanup to a 10^{-6} benzene risk level would be protective of TPH, since fate and transport processes could result in reduction of the initial high TPH (alkane) levels. PAHs, the primary TPH components in soil possessing significant toxicity (*i.e.*, chrysene), are present in relatively small concentrations in jet fuels, and are not expected to contribute extensively to TPH.

As an alternative to this approach, a simplified comparative analysis for one cubic yard of soil cleaned to a TPH cleanup level of 10 ppm or a BTEX (benzene) cleanup level of 22 ppm can be constructed.

In summary, the ability of an acceptable BTEX (benzene) soil cleanup level to result in an acceptable TPH soil level, and vice versa, is best presented at the site level with full consideration of individual site-specific factors.

Figure 4-1. Residential PRG, Soil Ingestion Noncarcinogenic Equation

$$THI = \frac{C \times 10^{-6} kg/mg \times EF \times IF_{soil/adj}}{R_fD_o \times AT \times 365 days/year}$$

$$C(mg/kg) = \frac{THI \times AT \times 365 days/year}{1/R_fD_o \times 10^{-6} kg/mg \times EF \times IF_{soil/adj}}$$

where:

Parameter	Definition	Default Value
C	Chemical concentration (mg/kg)	None
THI	Target Hazard Index	1.0
R_fD_o	Oral chronic R_fD (mg/kg/day)	Chemical-specific
AT	Averaging time (years)	30 years (equal to exposure duration, which is incorporated in $IF_{soil/adj}$)
EF	Exposure frequency (day/yr)	350
$IF_{soil/adj}$	Age-adjusted ingestion factor (mg-yr/kg-day)	114

Reduced Equation:

$$Risk\text{-}based PRG (mg/kg soil) = 2.7 \times 10^5 \ (R_fD_o)$$

Table 4-1. Soil Concentrations of Potential TPH Substitutes Associated With Maximum "Acceptable" Noncarcinogenic or Carcinogenic Human Health Effects From Soil Ingestion

Carcinogens:

Chemical	Oral Slope Factor $(mg/kg/day)^{-1}$	Soil Concentration (ppm)
Benzene	2.9×10^{-2}	22
Chrysene (PAH)	0.073	8.8

Noncarcinogens:

Chemical	Oral R_fD (mg/kg/day)	Soil Concentration (ppm)
Anthracene	3×10^{-1}	81,000
Ethylbenzene	1×10^{-1}	27,000
Fluoranthene	4×10^{-2}	10,800
Fluorene	4×10^{-2}	10,800
Naphthalene	4×10^{-2}	10,800
Pyrene	3×10^{-2}	8,100
Toluene	2×10^{-1}	54,000
Xylene	2×10^{0}	540,000

Figure 4-2. Residential PRG, Soil Ingestion Carcinogenic Equation

$$TR = \frac{SF_o \times C \times 10^{-6} kg/mg \times EF \times IF_{soil/adj}}{AT \times 365\, days/year}$$

$$C\,(mg/kg) = \frac{TR \times AT \times 365\, days/year}{SF_o \times 10^{-6} kg/mg \times EF \times IF_{soil/adj}}$$

where:

Parameter	Definition	Default Value
C	Chemical concentration (mg/kg)	None
TR	Target excess lifetime cancer risk	10^{-6}
SF_o	Oral slope factor $(mg/kg/day)^{-1}$	Chemical-specific
AT	Averaging time (years)	70
EF	Exposure frequency (day/yr)	350
$IF_{soil/adj}$	Age-adjusted ingestion factor (mg-yr/kg-day)	114

Reduced equation:

$$Risk\text{-}based\,PRG = \frac{0.64}{SF_o}$$

Figure 4-3. Commercial/Industrial PRG, Ingestion and Inhalation Noncarcinogenic Equation

$$THI = \frac{C \times 10^{-6} kg/mg \times EF \times ED \times IR_{soil}}{R_fD_o \times BW \times AT \times 365\,days/year} + \frac{C \times EF \times ED \times IR_{air} \times (1/VF) \times (1/PEF)}{R_fD_i \times BW \times AT \times 365\,days/year}$$

$$C(mg/kg) = \frac{THI \times BW \times AT \times 365\,days/year}{ED \times EF \times [((1/R_fD_o) \times 10^{-6} kg/mg \times IR_{soil}) + ((1/R_fD_i) \times IR_{air} \times (1/VF + 1/PEF))]}$$

where:

Parameter	Definition	Default Value
C	Chemical concentration (mg/kg)	None
THI	Target Hazard Index	1.0
R_fD_o	Oral chronic R_fD (mg/kg/day)	Chemical-specific
R_fD_i	Inhalation chronic R_fD (mg/kg/day)	Chemical-specific
BW	Adult body weight (kg)	70
AT	Averaging time (year)	25 (equal to ED)
EF	Exposure frequency (day/yr)	250
ED	Exposure duration (year)	25
IR_{soil}	Soil ingestion rate (mg/day)	50
IR_{air}	Inhalation rate (m^3/day)	20
VF	**Soil-to-air volatilization factor**	**Site, chemical-specific**
PEF	**Particulate emission factor (m^3/kg)**	**Site-specific**

Reduced Equation:

$$Risk\text{-}based\,PRG = \frac{102}{(5 \times 10^{-5}/R_fD_o) + ((1/R_fD_i) \times (20/VF)) + (1/PEF)}$$

Figure 4-4. Commercial/Industrial PRG, Ingestion and Inhalation Carcinogenic Equation

$$TR = \frac{(SF_o \times C \times 10^{-6} kg/mg \times EF \times ED \times IR_{soil})}{BW \times AT \times 365\,days/year} + \frac{SF_i \times C \times EF \times ED \times IR_{air} \times (1/VF + 1/PEF))}{BW \times AT \times 365\,days/year}$$

$$C(mg/kg) = \frac{TR \times BW \times AT \times 365\,days/year}{EF \times ED \times [(SF_o \times 10^{-6} kg/mg \times IR_{soil}) + (SF_i \times IR_{air} \times (1/VF + 1/PEF))]}$$

where:

Parameter	Definition	Default Value
C	Chemical concentration (mg/kg)	None
TR	Target excess lifetime cancer risk	10^{-6}
SF_o	Oral slope factor $(mg/kg/day)^{-1}$	Chemical-specific
SF_i	Inhalation slope factor $(mg/kg/day)^{-1}$	Chemical-specific
BW	Adult body weight (kg)	70
AT	Averaging time (year)	70
EF	Exposure frequency (day/yr)	250
ED	Exposure duration (years)	25
IR_{soil}	Ingestion rate (mg/day)	50
IR_{air}	Inhalation rate (m^3/day)	20
VF	Soil-to-air volatilization factor	Site, chemical-specific
PEF	Particulate emission factor (m^3/kg)	Site-specific

Reduced equation:

$$Risk\text{-}based\,PRG = \frac{2.9 \times 10^{-4}}{((5 \times 10^{-5}) \times SF_o) + (SF_i \times ((20/VF) + (1/PEF)))}$$

5.0 OPTIONS FOR RAISING A RISK-BASED SOIL CLEANUP CONCENTRATION FOR THE TPH SUBSTITUTE (BENZENE)

*Summary: Section **5.0** is focussed on how an appropriate preliminary remediation goal (PRG) is developed for benzene, the preferred TPH substitute in soil as determined in Section **4.0**. The two key elements considered in establishing the benzene PRG are the same two key elements used to establish human health risk: benzene's cancer potency factor and, quantitative expression of the potential for human exposure to benzene. Various ways of expressing both of these elements were explored in this section, including the use of Monte Carlo simulation. PRGs are site-specific because many of the factors used to calculate them vary from site to site and are necessarily dependent on conditions at a particular site. Therefore, site-specific PRGs were not calculated in Section **5.0**.*

Risk-based cleanup concentrations for a chemical of concern are derived from benchmark measures of toxicity (*e.g.*, R_fD) for the chemical and its site-specific exposure conditions. As discussed in **Sections 4.1 and 4.2**, the USEPA has developed methods for calculating "risk-based preliminary remediation goals" (PRGs) for Superfund sites (USEPA 1991a). This methodology involves solving the risk equation for the soil concentration term (*i.e.*, by back-calculating an "acceptable" concentration based on a predetermined "acceptable" level of risk). Thus, the factors that affect the cleanup level are: (1) the predetermined "acceptable" level of risk; (2) benchmark measures of toxicity; and (3) site-specific exposure parameters.

As benzene carcinogenicity is anticipated to drive the site risk estimates, the two major components specifically examined were alternative cancer slope factor (SF) determinations for benzene (*i.e.*, distributional analysis of dose-response relationships developed from cancer studies), and site-specific exposure reduction strategies (*i.e.*, distributional analysis of exposure estimates) that might be employed at Air Force JP-4 sites. These elements are discussed in the sections below.

5.1 Establishing a Predetermined "Acceptable" Risk Level

The target risk level for Superfund sites for carcinogenic effects is usually 1×10^{-6} (based on the NCP's point of departure for analysis of remedial alternatives) (USEPA 1991a). However, the interpretation of this "point of departure" is based on the following:

> *"For known or suspected carcinogens, acceptable exposure levels are generally concentration levels that represent an excess upper bound lifetime cancer risk to an individual of between 10^{-4} and 10^{-6}." (40 CFR Part 300)*

Thus, depending on site-specific conditions (*e.g.*, severity of biological effect, potency of the chemical of concern, size of the potentially exposed population, degree of potential future exposure based on future land-use projections), 10^{-5} or 10^{-4} may be more appropriate predetermined levels of "acceptable" risk. In addition, state-specific interpretations of "acceptable" risk may vary as well (*i.e.*, California, where "acceptable" equates to 10^{-5} risk levels), although nonCERCLA sites would be the best candidate sites where state jurisdiction takes precedence.

5.2 The Cancer Slope Factor

The general approach to formulating a cancer slope factor is presented below, along with the inherent uncertainties in its estimation. In addition, a specific discussion of the basis for the existing benzene cancer slope factor is presented.

5.2.1 Derivation of a Cancer Slope Factor

The USEPA has developed cancer slope factors for specific compounds whose cancer weights-of-evidence classifications are Categories A, B1, or B2[10]. Cancer SFs reflect the dose-response relationship between the dose of the chemical and (typically) tumor frequency. The SF represents a numeric estimate of the lifetime probability of a particular response (cancer) for a given unit dose of a chemical, although procedurally this dose is typically estimated by the USEPA as the conservative 95th percentile upper confidence level (the "upper bound") on the probability. There are several components to the derivation of the SF that can significantly influence the value of the SF, such as:

- Selecting and interpreting an appropriate data set as the basis for the SF;
- Extrapolating a response obtained at the exposure levels in the data set to a response at the more typical low-dose exposures anticipated to occur;
- Determining equivalent human doses from animal studies; and,
- Generating the upper-bound on the point estimate of the cancer SF.

The procedure for deriving a cancer SF is discussed below in the context of use of best professional judgement in applying these four components and the potential for variation among the components.

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[10] Category A = Known human carcinogen
Category B1 = Probable human carcinogen with human evidence
Category B2 = Probable human carcinogen with animal evidence

5.2.2 Selecting Appropriate Data Sets as the Basis for the Slope Factor

In establishing an SF, human epidemiologic or experimental data of good quality are invariably preferred over animal data. Practically, animal studies are utilized more extensively to generate SFs because exposures are more controlled and quantifiable and because adverse health endpoints are easier to measure. Animal species with greatest metabolic, physiologic, and pharmacokinetic similarity to humans are preferred, although more typically, dose-response data obtained from the most sensitive animal species are used because other desired information is lacking. Study results are weighted according to the strength of their experimental design and the quality of their results.

The accuracy and representativeness of the benzene dose-response relationship is affected by the number of experimental dose levels used, the number of animals exposed at each dose level, the route of exposure, the duration of the study, and the health endpoints examined. Typically, the "best quality" study is identified and then used as the basis for the SF. If no single study is identified as most appropriate, several studies may be considered to ensure that all relevant and applicable data have been utilized. Variations in any of these study parameters and in their interpretation can affect the derived SF.

5.2.3 High-Dose to Low-Dose Extrapolation

Results from human occupational studies and experimental animal studies are based on human exposures or experimental doses that are higher than those to which humans are usually exposed. The advantages to using higher exposures/doses is that they elicit observable, measurable responses in relatively small sample sizes. While adverse biological effects may be noted at higher dose levels, the correct manner for extrapolating experimental high-dose information to environmental low-dose exposures remains at issue. High-to-low-dose extrapolation typically involves the use of one of several mathematical models to "fit" the available data and extend the dose-response curve into the lower dose regions. The bases for these models range from simple estimations of dose-related probabilities derived from general premises about the mechanism of cancer formation, to more biologically-based models involving more complex interpretations of cancer mechanisms and chemical-specific information.

Different models exhibit different degrees of fit with respect to the study data, and while the relative differences in fit may be scientifically acceptable, the resulting predicted response levels (cancer frequencies and their associated risks) at low doses may vary considerably.

The USEPA typically uses the linear multistage model (LMS), which incorporates current assumptions about the mechanism of cancer formation, in addition to a "goodness of fit" approach to the study data.[11] LMS is used preferentially by the USEPA when there is limited information on the actual mechanism of cancer formation, because it derives a more conservative SF (*i.e.*, it predicts a higher SF), and yields correspondingly higher risk estimates.

5.2.4 Deriving the Equivalent Human Dose of Benzene

When animal data are used as the basis for the human SF, doses given to the animals must subsequently be mathematically converted for applicability to humans. This conversion is based on the premises that:

- Absorbed doses are the same from species to species within the same unit of body surface area; and,
- The approximate mathematical relationship between surface area and body weight is:

$$Surface\ Area = Body\ Weight^{\frac{2}{3}} \tag{1}$$

$$Human\ Dose = Animal\ Dose\ x\ [\frac{Human\ Body\ Weight}{Animal\ Body\ Weight}]^{\frac{2}{3}} \tag{2}$$

Typically, for inhalation studies involving partially soluble/absorbed gases, the air concentration to which the animal is exposed (*i.e.*, ppm) is considered the equivalent human dose (given equal exposure times). For gases which are completely absorbed, the amount absorbed per unit of body surface area is considered equal.

Human equivalent-dose conversion is controversial. It has been proposed, for example, that equivalent doses be obtained using a direct body weight-based approach rather than a surface area-based approach (USEPA 1992), where

$$Human\ Equivalent\ Dose = Animal\ Dose\ x\ [\frac{Human\ Body\ Weight}{Animal\ Body\ Weight}]^{\frac{3}{4}} \tag{3}$$

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[11] The basic assumptions are that: (1) the mechanism of cancer involves a series of stages in a cell's progression toward becoming a tumor cell, and (2) the low-dose-response region of the dose-response curve is linear.

5.2.5 Presenting the "Upper Bound" Slope Factor

Once the dose-response data have been fit to the chosen model, the slope of the low-dose-response curve is estimated, and the upper 95th percentile confidence limit (upper bound) on this estimate is calculated. This upper-bound on the cancer SF represents a conservative 95 percent probability on the cancer dose-response relationship. In some cases, as with human data used for generating a cancer SF, the best estimate (*i.e.*, the maximum likelihood estimate, MLE) for the cancer SF is used, without its 95 percent upper bound, to reflect increased certainty in the cancer dose-response relationship derived from human data.

Use of the upper-bound estimate in lieu of the MLE can lead to an overestimation of risk. A single value for the cancer SF limits the interpretation of the risk estimate derived from the SF. An alternative procedure for crafting a SF that permits a broader inclusion of available scientific data involves calculating a *range or distribution* of cancer SFs. This approach permits the expression of variabilities in:

- Different dose-response data sets;
- Different assumptions about the mechanisms of cancer formation;
- Different methods for estimating human dose equivalence; and,
- Different low-dose extrapolation models.

The implications of applying these variabilities to the calculation of the benzene cancer SF are presented in the next section.

5.3 Distributional Analysis of Dose-Response Relationships Developed from Cancer Studies

The derivation of the benzene cancer slope factor is presented below, with its accompanying uncertainties. The potential for alternative procedures and estimates is also discussed.

5.3.1 Derivation of the Benzene Cancer Slope Factor

The USEPA's approach to deriving the cancer SF for benzene (USEPA 1985) is based on consideration of data obtained primarily from <u>three</u> epidemiology studies of workers exposed to benzene occupationally via inhalation (Ott *et al.* 1978; Rinsky *et al.* 1981; Wong *et al.* 1983). In all studies, the critical endpoint was cancer mortality attributable to leukemias. Information regarding the concentrations of benzene and durations of exposure were used to generate "dose groups" with benzene-related leukemia mortalities associated with each group, which were then used to derive dose-response curves. Finally, different cancer risk models were combined with different exposure parameters to generate cancer unit risks.[12]

Six different combinations of exposure model and risk model were used to generate benzene unit risks, depending on the magnitude of exposure and the type of risk being modeled. The six combinations were based on:

- Three models of benzene exposure:
  - Cumulative exposure;
  - Weighted cumulative exposure; or
  - A window of exposure.

  These exposure parameters were meant to encompass all potential permutations of cancer latency, where latency was defined as the time to onset of tumor or death. They allowed for the risk of benzene cancer mortality to rise or fall proportionally with benzene concentration and exposure duration.

- Two risk models:
  - A *relative* risk model, where risk values could be estimated relative to the background leukemia incidence or the leukemia incidence of a control population; or

  - An *absolute* risk model, where risk values were not expressed with respect to the background or control leukemia incidence.

The two risk models (and their associated risk estimates) were applied to each of the three exposure models, yielding six possible combinations of conditions/models under which to estimate benzene cancer SFs. For each one of the six combinations, several variations of the three data sets from the three epidemiology studies were used to calculate the slopes of the respective low-dose-response curves[13], resulting in 21 dose-response combinations of models and data sets. From the 21 dose-response curves, 21 maximum likelihood estimates (MLEs)[14] and upper and lower bounds on these MLEs were generated. MLEs were then presented for the risk at the unit dose of 1 ppm (unit cancer risks, ppm^{-1}). These MLE unit cancer risks ranged from 8.98×10^{-3} ppm^{-1} to 1.04×10^{-1} ppm^{-1}, an 11-fold variation (over 1 order of magnitude). The actual distribution of these initial unit cancer risk estimates is shown in **Figure**

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[12] The risk associated with a unit dose of benzene equal to 1 ppm.

[13] Typically the variations involved extending the length of followup time for the populations, thereby altering the frequencies of mortalities associated with each exposure group.

[14] The actual fitted data estimates.

5-1. In order to obtain a representative estimate of the MLE, four MLEs from the 21 MLEs were chosen, thought to be the best approximations based on:

- Use of the two best common data sets (Ott *et al.* 1978 and Rinsky *et al.* 1981),
- Excluding estimates for "window" doses, and
- Giving equal weight to each of the risk/exposure (dose) models:
    - Relative risk-cumulative dose
    - Absolute risk-cumulative dose
    - Relative risk-weighted cumulative dose, and
    - Absolute risk-weighted cumulative dose.

The four MLEs ranged from 1.04×10^{-2} to 2.89×10^{-2}, a two-fold variation. The geometric mean of these four unit cancer risks was estimated (2.11×10^{-2}), and subsequently modified by a factor (1.23) which reflected an adjustment for comparative consideration of the Wong study (1983), to yield a final unit risk estimate of 2.6×10^{-2} ppm^{-1}. This unit cancer risk value was converted by USEPA to an oral SF of 2.9×10^{-2} (mg/kg/day)$^{-1}$ (the value shown in **Table 3-5**), using standard conversion methods[15] (USEPA 1989).

Animal data were considered to be a secondary and less germane source of information for estimating the benzene cancer SF. Several studies examined (Goldstein *et al.* 1980; Maltoni *et al.* 1983; NTP 1984) were based on inhalation or oral gavage routes. When endpoints from the animal inhalation studies related to leukemia were used to generate unit cancer risks, all unit risk values were less than those obtained from human epidemiology data (indicating less associated risk). Gavage studies generally yielded higher unit risk estimates, based on nonleukemia endpoints such as tumors of the preputial gland. However, preputial glands are only found in rats, and the exposure route was not similar to the epidemiology studies. Therefore, this endpoint was not considered to be directly applicable to estimates of human risks.

Sensitivity analysis[16] was explored by the USEPA as a method for examining the inherent variation within the animal inhalation unit cancer risk estimates. Assumptions that were explored included:

- Using the LMS model or a second model, the LMS-Weibull model (to compensate for animal mortality prior to the end of the study);

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[15] Conversion assumes 1 ppm benzene = 3.26 mg/m^3; adult body weight = 70 kg; adult inhalation rate = 20 m^3/day.

[16] The effect produced on the final unit risk value when one variable or pair of variables (assumptions) are altered, while keeping all other parameters constant.

- Generating the MLEs of unit risks or the 95th percentile upper bound unit risk values; and

- Converting from animal to human equivalent dose using either a surface area proportionality or a body weight proportionality.

The results indicated that regardless of which dose equivalence method was used, use of one model versus the other model yielded a variation of only two-fold in the final unit cancer risks (for MLE or 95th percentile upper bound estimates). The greatest variation between unit cancer risks generated (an order of magnitude (12-fold) difference) occurred with each of the two risk models, using the same model with different human dose-equivalence methods.

5.3.2 Uncertainties Associated with the Benzene Cancer SF

- Human exposure groups were defined according to broad categories of exposure, based on duration and concentration of exposure (in contrast to animal studies, for example, where doses are discrete and precise). Each human exposure group (category) contained numerous combinations of exposure concentration and duration; individuals were placed within a given category. Individual group distributions and variabilities, as well as where on the distribution continuum most of the exposure occurred, were unknown.

- Exposures were known or grouped partially on the basis of the benzene air concentration to which an individual was exposed. Therefore, the benzene air concentration effectively acts as an *external* dose. There is no compensation for the percent of benzene absorption after inhalation, which yields an *internal or biological* dose.

- The estimation and use of the two categories of the exposure parameters[17] also carries associated uncertainty. In cumulative exposure:

$$\mathit{Risk} \propto \sum [\mathit{Exposure\ Duration}\ x\ \mathit{Time}] \qquad (4)$$

In *weighted* cumulative exposure:

$$\mathit{Risk} \propto \sum [\mathit{Exposure\ Duration}\ x\ \mathit{Time}\ x\ \mathit{Leukemia\ Latency}] \qquad (5)$$

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[17] Either (1) Cumulative exposure (total lifetime exposure in ppm-years), or (2) weighted cumulative exposure (total lifetime exposure in ppm-years, but weighted for the relative prior duration of exposure).

Both proportionality assumptions were given equal weight in the final estimation of the cancer SF for benzene, given the uncertainty of the relative accuracy of either one.

- The use of models that estimate *relative* risk versus *absolute* risk also carries uncertainty:
  - *Relative* risk assumes that benzene leukemia occurs via the same mechanism as "other" (*i.e.*, nonbenzene-associated) leukemias observed in the background group (general population or control group). Therefore, the benzene-associated leukemia risk (or benzene-associated leukemia mortality rate) is proportional to the overall leukemia background rate and should follow the same trend (to increase over time/age) as the background leukemia rates.
  - *Absolute* risk is not based on the assumption of a similar mechanism or trend for benzene-associated leukemia mortalities.

  Since it was not clear which of the two risk models is more appropriate, equal consideration was given to each model. Relative risk models were employed for two of the four unit cancer risk values used for the SF, while the other two used absolute risk as the model.

5.3.3 Alternate Methods for Characterizing the Benzene SF

Methods that are employed or suggested in presenting the uncertainty inherent in estimates of risk included sensitivity analysis and Monte Carlo simulation. These methods and a more novel approach, information analysis, are discussed in the following paragraphs.

A sensitivity analysis on the SF, the application of which was described in **Section 5.3.1** (Derivation of the Benzene Cancer Slope Factor), is a method for detecting the relative effects of altering the assumptions or parameters used to derive the SF. The method involves altering one factor while holding all others constant. By systematically altering each variable separately, the variable that will result in the greatest magnitude of change in the SF can be identified as a sensitive parameter. This process defines the range over which the final SF can vary according to the variation in a single input parameter.

> Applying this approach to the relative risk model for cumulative exposure in the benzene SF estimation (one of the six modeling approaches described above), the same data set is used three times, except that in each cycle the followup time for the population of interest has been increased by approximately ten years. In essence, this is a sensitivity analysis of the effect of modifying followup time (or latency time) on the MLE of the benzene SF.

While such an approach can be applied to the benzene SF, it yields limited information beyond the SF range attributable to one or two individual parameters.

Monte Carlo simulation is more sophisticated approach, in that it allows for some estimation or deduction of the variation in the cancer SF when multiple input variables are altered. For application to the benzene SF, the following parameters must be known:

- The "correct" combinatorial risk model to apply (absolute or relative; cumulative or weighted cumulative exposure), and
- Distributions or the lower and upper bounds on these and other parameters.

A distributional approach for a single model is very difficult unless the following information is present:

- Specific mechanistic information on benzene carcinogenesis;
- Understanding of the latency of benzene-induced leukemia from inhalation exposure; and,
- Epidemiologic trends in mortality rates.

Information analysis (Sielken 1991a,b) is a recently developed alternate weight-of-evidence technique for presenting the benzene SF distribution. This approach depicts the variation in the SF from the point-of-view of the "most likely" scenario(s), yet does not require knowledge of the specific mechanisms or distributions. The weight-of-evidence approach involves three major steps:

- Generating a series of options for input parameters;
- Applying weight-of-evidence to support the degree to which each input parameter is "correct" (*scientific truth*); and,
- Applying weight-of-evidence for each potential path used to model the unit risk value.

This is a means for adjusting individual MLEs that are generated by any one of several methods, so that each individual MLE reflects the best available knowledge on both the chemical and the SF methodology. The end result is a distribution of weighted SFs.

For example, the major parameters for the various stages in formulating the SF that require characterization in deriving an SF include:

- *The human carcinogenic response.* What is the carcinogenic weight-of-evidence for a specific route of exposure?
- *Mode of action.* What is the chemical-specific mechanistic information? Is the chemical genotoxic, a proliferation-inducer, or both?

- *Dose scale.* Are doses presented as administered, delivered, or biologically effective?
- *Dose-response model.* What model is being used: quantal (*e.g.*, probit, logit, Weibull, multihit, multistage), time-to-tumor (*e.g.*, multistage-Weibull, Weibull-Weibull, Hartley-Seilken, Armitage-Doll), or growth (*e.g.*, two-stage MVK)?
- *Experimental data set.* What are the specific features of the data set on which the SF is based (*e.g.*, study design, route, species, response)?
- *Interspecies extrapolation method.* Is the extrapolation from animals to humans according to body weight or surface area?

All possible permutations of the choices are represented, and are depicted as branches on a tree, where each fork is the next stage at which a choice is made. For each major input parameter (mode of action, dose scale, model type, *etc.*), all possible choices are considered for how well they reflect the current state of knowledge or "truth", with respect to the choices/inputs made prior to that point, and are given a proportional weight-of-evidence[18]. Each pathway then has a series of weights associated with each component, all of which are then multiplied together to yield the final weight for the particular pathway or final branch. The unit risk for each possible pathway is estimated as the MLE, with its associated weight-of-evidence that represents the probability that this MLE reflects a true risk estimate, yielding a distribution of weighted MLEs.

The potential for the application of the weight-of-evidence approach to substantially alter the benzene SF is questionable. This type of approach has the advantage of not requiring that any hypothesis be proven wrong (*i.e.*, there is no need to know the "correct" model to use, since it assigns weights that are relative to one another for all permutations that yield unit-risk MLEs). However, this method does require expert knowledge of all stages in the SF derivation and benzene-specific applications therein, and expert judgments that are made may require rigorous substantiation at all stages in the decision tree process.

5.3.4 Lack of Anticipated Appreciable Alteration in Benzene SF

Based on the current USEPA documentation on the derivation of the benzene SF (USEPA 1985), the potential for appreciably altering the benzene cancer SF is not anticipated to be significant. The following points address aspects in SF development that have traditionally been sources of considerable variation in deriving and interpreting SFs, and particularly those associated with the benzene SF derivation. Reference to more recent studies that have examined the USEPA approach are made as well, within the context of their applicability to lowering the cancer SF for benzene.

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[18] Note that the sum of these values equals one, since they are probabilities of being "correct".

- Unlike the majority of chemicals for which SFs have been derived, the benzene cancer SF was estimated from existing human epidemiology data. Hence, there is no variation associated with the interspecies extrapolation from animals to humans for which to account. In addition, peer review suggests that the studies used in setting the SF were the best available human studies.

- The benzene cancer SF was estimated using two different lifetime cancer risk models (relative and absolute risk) and two different assumptions of the appropriate exposure parameter (cumulative and weighted-cumulative exposure). While variation exists solely on the basis of the use of four estimates derived in four different manners, the extent of this variation is only two-fold, and the value is believed to encompass all potentially viable options. The traditional linear multistage model (LMS), with its inherent conservative estimation of cancer SFs relative to other models, was not used by the USEPA in the derivation of the benzene SF.

- The benzene SF was presented as the geometric mean of the maximum likelihood estimates (MLEs), as opposed to the more standard approach used for the majority of SFs, which is to present the SF as the 95th percentile upper bound. The use of the upper bound versus the MLE would yield a SF greater than the MLE, with the variation between the MLE and the upper bound being substantially greater than the variation between the four MLE estimates used to establish the benzene SF.

- In light of recent increased understanding of several parameters employed in the estimation of the benzene SF, a study was designed to quantitatively reevaluate the USEPA estimate of the benzene SF (Clement 1988). The study proposed that the benzene cancer SF could effectively be decreased by an order of magnitude (Clement 1988). At this time, the extent to which this report has been reviewed, either by external peer review or the USEPA, has not been directly ascertained, although USEPA personnel indicate that there has been no study to substantially refute the currently established SF.

5.4 Alternative Methods for Determining Exposure Estimates

The USEPA risk assessment methodology for exposure assessment suggests a series of standard default exposure routes and exposure assumptions/parameters for use in conjunction with discrete current and future land use scenarios. While the exposure routes themselves may be more or less applicable to a specific site, the majority of the standard exposure assumptions advocated for use in estimating chemical intakes are not site-specific, nor are they necessarily the most current, relevant numerical values. Historically, the use of alternate *standard* assumptions or the development of site-specific assumptions has been met with varying degrees of acceptance by regulatory agencies, although the existing guidelines for these assumptions (USEPA 1989, 1991b) and the guidelines regarding the formulation of site-specific PRGs (USEPA 1991a) advocate the use of site-specific information wherever possible. Site-specific information and viable exposure routes will vary with the location, magnitude, and nature of the spill or leak, as well as the local human populations, regional topology and hydrogeology, and land use. Some practical, site-specific considerations are discussed below.

5.4.1 Use of Site-Specific Exposure Parameters

The potential for exposure of humans who come in contact with the site of a former JP-4 spill or leak can be influenced by factors such as: *the identification of the current and future land uses at the site* (*e.g.*, current land use which is active, inactive, industrial, residential, or agricultural; future land use which is similar to current, or involves conversion to industrial, residential, or agricultural); *the identification of the human receptor of greatest concern* under these land uses (*e.g.*, a worker in an industrial setting, a child in a residential setting, a farmer in an agricultural setting); *the physical nature of the site* (*e.g.*, heavily vegetated, bare topsoil, pavement, limited geographical access, fenced, distance to a potable aquifer; geological stratification); *the size/volume of the spill or leak*; and, *the age of the spill or leak.* Based on knowledge of such conditions, realistic assessments of potential routes for exposure can be made. Knowledge of the fate and transport of JP-4 constituents will assist in making educated and experienced exposure route assessments. The establishment of a realistic route of exposure for a site lends greater strength to any soil remediation criteria that may be developed using these exposure routes. This, in turn, ensures that the soil cleanup criteria will accurately reflect the risk at the site. Site-specific considerations and the use of site-specific exposure parameters, whenever feasible, are crucial to this process.

Most exposure estimates and risk calculations are a multiplicative combination of exposure assumptions resulting in a point estimate for the intake of a chemical. A "traditional" practice is to choose a combined variety of average, conservative, and worst-case standard assumptions. There are three disadvantages to this approach:

- There is no way of knowing the actual degree of conservatism in an assessment (*i.e.*, no realistic depiction of the variation can be presented for the exposure estimate, and hence for the ultimate risk level);

- By selecting upper limits on many exposure variables, the assessment generally considers scenarios that will rarely occur (*e.g.*, what is the likelihood of an individual ingesting the maximum soil amount per day, for every day of the maximum number of exposure days, for the maximum number of years the individual could live near site?); and,

- Sensitivity analyses are of limited value since many of the variables are at or near their maxima.

An alternative approach to the use of conservative assumptions is an exposure distributional analysis, in which ranges or distributions of individual exposure parameters (*e.g.*, the distribution of adult body weights) are considered to produce an overall distribution of potential exposure. A Monte Carlo simulation[19] is such an analysis.

5.4.2 The Monte Carlo Approach

Monte Carlo simulation is a procedure for solving problems involving random variation (chance or probability) where time does not play a major role (Law and Kelton 1982; Hillier and Lieberman 1986). It is widely used within the statistics community for certain types of problems that are not amenable to solution by experimentation (*e.g.*, estimating critical values, estimating the power of a new hypothesis test, estimating the effect of uncertainty on complex systems). Monte Carlo simulation has been used by statisticians, systems analysts, and engineers for many years, but its use in human health risk assessment is relatively recent (*e.g.*, Burmaster *et al.* 1990; ENVIRON 1991; Burmaster and von Stackelberg 1991; Hawkins 1991; RiskFocus 1990, 1991a,b).

Rather than using point estimates in exposure assessment, Monte Carlo simulation can be used to estimate distributions for exposure assumptions. Use of this methodology does not alter the basic structure of the exposure estimate as first described by the National Research Council (1983). However, it does refine the way chemical intakes are calculated in the exposure assessment.

In both the "traditional" and Monte Carlo approaches to exposure assessment, the analyst first constructs a model consisting of relationships between random variables [*e.g.*, the model for intake of a compound via ingestion of water (USEPA 1989, Exhibit 6-11, page 6-35)]:

$$Intake = \frac{CW \times IR \times EF \times ED}{BW \times AT} \qquad (6)$$

where:

$Intake$ = Intake (mg/kg/day)
CW = Chemical concentration in water (mg/L)
IR = Ingestion rate (L/day)
EF = Exposure frequency (days/year)
ED = Exposure durations (years)
BW = Body weight (kg)

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[19] There are three classes of methods generally used for simulating exposure under uncertainty: (1) sensitivity analysis; (2) probabilistic error propagation; and (3) fuzzy sets. Monte Carlo simulation is in the class of probabilistic error propagation (Lipton *et al.* 1992).

AT = Averaging time (days)

In the "traditional" approach to risk assessment, point estimates for each of the variables in the intake equation are chosen (*e.g.*, the 95th percentile upper confidence limit on the mean of the ground water sample concentrations; the 90th percentile of the distribution of adult water consumption). This results in a point estimate for intake which, having used conservative estimates for each variable, suggest an intake quantity that is doubly indemnified by using 90th and 95th percentiles in its derivation. Because different percentiles were used[20], it is not possible to know what *combined* percentile to assign to the overall expression of intake.

In a Monte Carlo simulation model, the analyst determines a continuous or discrete distribution to describe each of the random variables in the model's equation. This distribution is defined in terms of the probability density function (PDF) or the cumulative distribution function (CDF). In the case of a normal distribution, the distribution is completely defined by specifying two parameters: the mean and variance. An entire family of normal distributions is generated by varying the mean and/or the variance. Other distributions are defined by one, two, or more parameters.

When running a Monte Carlo simulation model, the computer randomly "draws" one value from the appropriate distribution for each of the random variables in the model. For example, the computer randomly selects a chemical concentration from the chemical's distribution of concentrations, an ingestion rate from the distribution of ingestion rates, and other parameters necessary to solve **Equation 6**. The model then calculates a human daily intake according to **Equation 6**. This variable selection and computation process is repeated thousands of times to provide a distribution of daily intakes. The distribution is often bell-shaped (*i.e.*, a normal distribution) or skewed to the right. From this distribution, a specific intake can be selected (*e.g.*, the average or mean intake, median intake, or 95th percentile upper confidence limit on the intake) that, in combination with the appropriate toxicity benchmark concentration, is used to calculate risk.

In addition, a Monte Carlo simulation can include correlations between variables (Smith *et al.* 1992). For example, there is a correlation between body weight and ingestion rate. Using strongly correlated variables in deriving an estimate of exposure serves to strengthen the estimate by preventing nonsensical combinations of variables in its derivation.

In most cases, the daily human intake calculated using Monte Carlo simulation is less than that calculated using point estimates. This is not to suggest the use of Monte Carlo simulation because it produces lower estimates, but rather because its estimates can be associated with probabilities. This results in increased confidence in the estimate of intake, thus ensuring increased confidence in public health protection.

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[20] In some cases *no* distribution-based percentiles are used, such as an exposure frequency of 350 days per year based on the assumption that people are away from home two weeks per year.

5.5 Distributional Analysis of Exposure Estimates

The identification of the essential components of an exposure analysis and their application within a Monte Carlo-based approach are discussed in the following sections.

5.5.1 Critical Components of the Exposure Analysis

One means to deriving exposure estimates is to use a Monte Carlo simulation to yield a distributional analysis of exposure estimates. The objective of the exposure analysis in the risk assessment process is to estimate the magnitude, frequency, and duration of human exposures to a chemical present in the environment. A complete exposure estimate, then, would characterize the route, duration, and magnitude of exposure; the populations exposed, including sensitive populations; and the uncertainties associated with all estimates. The critical components of an exposure analysis have thereby been delineated as:

- Analysis of data,
- Evaluation of transport, migration and distribution of chemical constituents,
- Identification of all exposure routes and potentially exposed populations, and
- Estimation of exposure parameters (to include, but not be limited to: soil ingestion rates, dermal contact rates, inhalation rates, and bioavailability issues) (Michaud *et al.* 1991).

Each of these components is used in some manner in the resulting exposure estimate (*e.g.*, the analysis of data is used to estimate media-specific chemical concentrations; transport and migration are used to evaluate potential exposure points; the exposure parameters are used in the actual mathematical calculations). However, those components critical to the Monte Carlo simulation are the parameters used in the mathematical calculations.

A recent workshop cosponsored by USEPA and the University of Virginia attempted to: (1) assess the state of the art in selecting input distribution functions, with an emphasis on their applications to environmental risks; and (2) establish theoretically sound and defensible foundations upon which to generate future guidelines for USEPA use in the selection of probability distributions (UVA 1993). The issue papers and workshop participants concluded that the selection of the input distributions are critical and attempted to propose means to advance the state of the art. There was no consensus on the use of specific distributions, the exception being mutual agreement on the need for use of scientifically defensible, rationally chosen, <u>site-specific</u> distributions.

Thus, the selection of input distributions for exposure assessment at a JP-4-contaminated site must be made based on site-specific conditions. This need for site-specificity incorporates all of the critical components listed above, including choice of appropriate exposure pathways and sensitive subpopulations.

5.5.2 Application of the Monte Carlo Approach

For example, at a hypothetical site it is determined that ground water is the medium of concern and offsite residents are the population of concern based on their use of ground water as a drinking water source. Use of exposure estimation equations yields an estimation of intake for ground water. Typically this would result in a point estimate. Using a distributional analysis, a distribution of intakes would be estimated. **Figure 5-2** presents the input distribution variables used in a hypothetical estimation of intake for benzene in drinking water, while **Figure 5-3** presents the input for deriving the standard, point estimate. As can be seen from **Figure 5-4**, the resulting point estimate of the lifetime average daily dose (LADD), 4.11×10^{-2} mg/kg/day, corresponds to greater than the 95th percentile on the distributional analysis (offscale). If, instead, the 95th percentile was of interest, the resulting estimate from the distributional analysis would be 1.7×10^{-2} mg/kg/day, a lower exposure estimate. In addition, if the cancer risk estimate includes a simple distributional analysis of the slope factor, in this case assumed to be lognormal, the effect of the distributional analysis is even greater (**Figure 5-5**). The cancer risk estimated by use of the point estimate LADD and the benzene SF is 1.19×10^{-3} (essentially 1×10^{-3}) (**Figure 5-3**), while the 95th percentile for the cancer risk based on the distributional analysis (**Figure 5-5**) would predict 3.8×10^{-4} (essentially 4×10^{-4}).

In another example, Lloyd *et al.* (1992) used a Monte Carlo simulation to evaluate the New Jersey Department of Environmental Protection (NJDEP) approach for calculating surface soil cleanup standards for benzene. The authors considered only a soil ingestion pathway. The NJDEP point estimate for the benzene cleanup concentration is 3 mg/kg, which is well below the 1st percentile of the overall distribution determined by Lloyd *et al.*, and thus a very conservative value.

Figure 5-1. Benzene Unit Risks
Frequency Distribution (USEPA 1985)

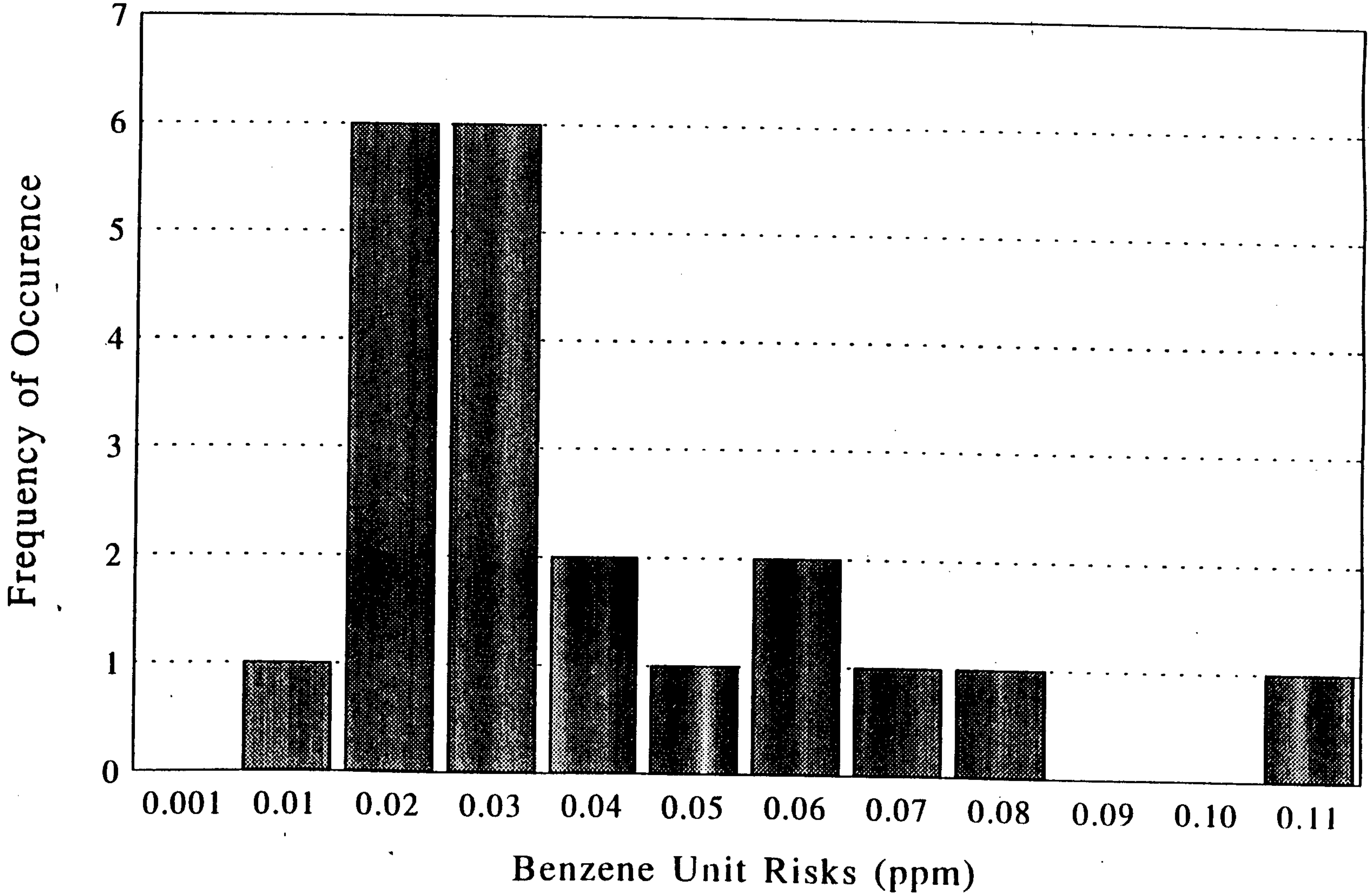


Figure 5-2. Estimating a Distribution of Human Daily Intakes

Scenario: Ingestion of benzene in water

$$LADD = \frac{C \times IR \times EF \times ED}{BW \times LS \times CF}$$

where:

LADD = Lifetime Average Daily Dose (mg/kg/day)
C = Concentration (mg/liter)
IR = Ingestion rate (liters/day)
EF = Exposure frequency (days/year)
ED = Exposure duration (years)
BW = Body weight (kg)
LS = Life span (years)
CF = Conversion factor (365 days/year)

$$Cancer\ risk = LADD \times CPF$$

where:

LADD = Lifetime Average Daily Dose (mg/kg/day)
CPF = Cancer potency factor $(\mathrm{mg/kg/day})^{-1}$

Input distributions:

C	Triangular (minimum = 0.25, most likely = 1.0, maximum = 1.5)	
IR	Normal ($\mu = 1.3$, $\sigma = 0.25$)	
EF	Triangular (minimum = 250, most likely = 350, maximum = 365)	
ED	Triangular (minimum = 9, most likely = 30, maximum = 70)	
BW	Equal chance of selecting male or female body weight	
	Male (ln lb):	Lognormal ($\mu = 5.14$, $\sigma = 0.17$)
	Female (ln lb):	Lognormal ($\mu = 4.95$, $\sigma = 0.21$)
CPF	Lognormal ($\mu = -4.33$, $\sigma = 0.67$) of underlying normal	

Figure 5-3. Calculating LADD and Cancer Risk Using Point Estimates

Point estimate:

$$LADD = \frac{1.5\,mg/\ell \times 2.0\,\ell/day \times 350\,days/year \times 70\,years}{70\,kg \times 70\,years \times 365\,days/year} = 4.11 \times 10^{-2}\ mg/kg/day$$

$$Cancer\ risk = 4.11 \times 10^{-2}\,mg/kg/day \times 0.029\,(mg/kg/day)^{-1} = 1.19 \times 10^{-3}$$

Figure 5-4. Point Estimate and Distribution of a Groundwater to Drinking Water LADD

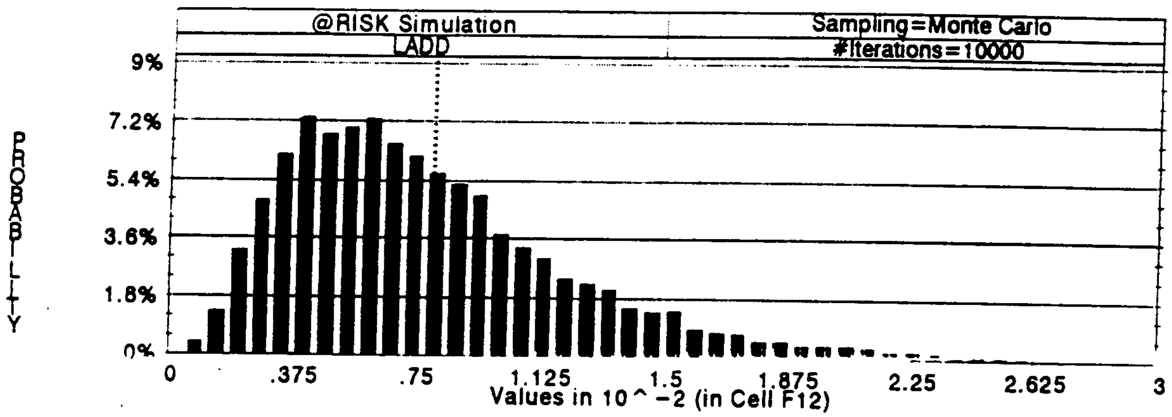
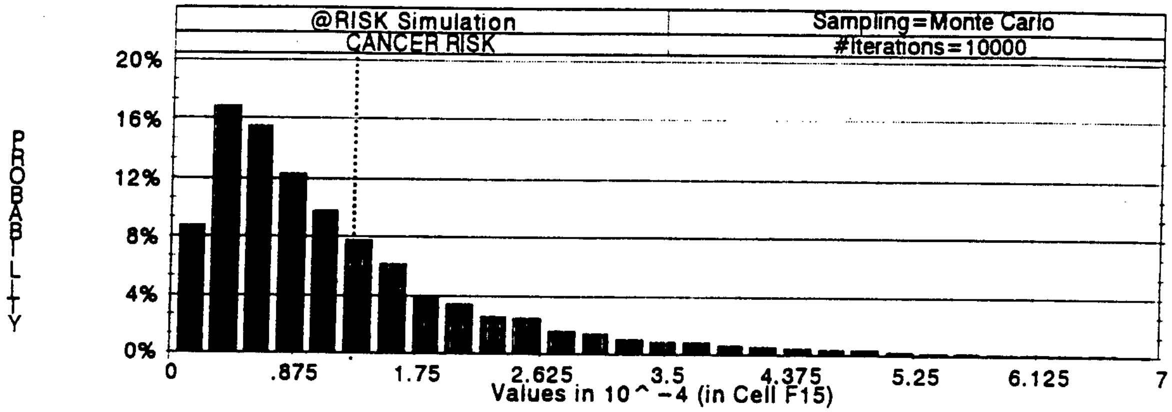


Figure 5-5. Point Estimate and Distribution of a Groundwater to Drinking Water Cancer Risk



6.0 CONCLUSIONS AND RECOMMENDATIONS

The following conclusions constitute the results of analyses performed throughout this report:

- There is no established USEPA regulatory policy for BTEX or TPH soil cleanup concentrations, to date.
- There is ongoing USEPA work towards establishing guidelines for soil cleanup concentrations based on protection of ground water.
- There are variable state-specific approaches to setting BTEX and/or TPH soil cleanup levels
- State-specific soil cleanup concentrations for BTEX are based primarily on protection of human health via protection of ground water, and/or protection of health for the soil ingestion route.
- State-specific soil cleanup concentrations for TPH are based primarily on consideration of one or more BTEX components in specific fuels, and extrapolation to TPH concentrations, as well as increasingly nonscientific approaches.
- Among all potential substitutes for TPH at JP-4 spill sites, benzene (BTEX) appears to be the most appropriate substitute based on its toxicity (carcinogenicity), weight-of-evidence cancer classification (Category A carcinogen), motility in the environment, ubiquity at JP-4-contaminated sites, and potential for migration to ground water.
- Based on these parameters, risk-based soil cleanup concentrations based on BTEX tend to be driven by benzene.
- Risks associated with exposure to benzene in ground water used as a drinking water source is anticipated to dominate risks for benzene in other media.
- Risk-specific concentrations for benzene (and other BTEX constituents) can be developed in soil, ground water, and other media.
- Remediation to a benzene soil cleanup concentration will not necessarily achieve simultaneous TPH soil cleanup.
- Benzene cancer risk is determined from the benzene slope factor and potential for exposure. Factors influencing the slope factor include the experimental data set used in its derivation, method of low-dose extrapolation, interspecies (animal to human) extrapolation, and use of the upper bound on the slope factor instead of the maximum likelihood estimate.

- The potential for appreciably altering the benzene cancer slope factor is not anticipated to be significant.

- There is no scientific consensus on use of specific distributions. However, scientifically defensible, rationally chosen, site-specific distributions should be used to estimate exposure.

The following recommendations are the outcome of the conclusions of these analyses as well as additional considerations:

- Benzene should be adopted as the TPH substitute;

- Research and funding efforts should focus on formulating site-specific soil cleanup concentrations for benzene, based on protection of ground water;

- A cost-benefit analysis should be undertaken for soil remediation of benzene and TPH, using current, acceptable remediation methods, and applying a site-specific approach; and,

- Research and funding efforts should be directed towards characterizing TPH, including chemical characterization, health effects, fate and transport, and the utility of TPH in the risk assessment process.

APPENDIX A

Approaches Used By States to Regulate BTEX

APPENDIX A
APROACHES USED BY STATES TO REGULATE BTEX

California

The State of California develops site-specific remediation goals according to the procedure described in its LUFT Manual (State of California 1989). This approach begins with a "Leaching Potential Analysis," which is used for initial site screening. Tank and piping samples are analyzed for TPH and BTEX; geologic site characteristics, such as soil type and permeability, are taken into account. Detected concentrations are compared to allowable concentrations for a site with the same geologic attributes. The matrix of allowable concentrations for various geologic site conditions was developed using fate-and-transport computer modeling. If the detected concentrations exceed the allowable concentrations, further study is warranted and a "General Risk Appraisal" is performed. The "General Risk Appraisal" involves the development of a soil contamination profile, in which soil borings are done, boring logs made, and soil samples are taken every five feet and analyzed for TPH and BTEX. Depth-specific contaminant concentrations and geologic attributes of the site are incorporated into computer models SESOIL and AT123D to arrive at site-specific cleanup goals for BTEX which represent the amount of contaminants which may be present in the soil under a similar site scenario and not cause drinking water standards to be exceeded at a point ten meters down gradient at the top of the aquifer (Daugherty 1991). Acceptable TPH levels are estimated by dividing the acceptable BTEX soil levels by the composition percentage in fuel. After remediation has been completed and the cleanup goals met, a human health risk assessment may be performed to ensure that public health will not be threatened by the site in the future. If groundwater had been impacted, a groundwater monitoring program may be required to asses the long-term effectiveness of the remedial action.

Colorado

Colorado, like California, has only remediation goals for the remediation of petroleum-contaminated soils; no enforceable regulations exist (LaRoca 1993). For both TPH and BTEX, remediation goals were formulated for three different levels of stringency by analyzing cleanup levels other states have implemented and picking "reasonable" values. These three levels are called Remedial Action Categories (RACs): Level 1 (most stringent) is for groundwater which functions as a public water supply, present or future; Level 2 is for groundwater which functions as a private water supply, present or future; Level 3 (least stringent) is for groundwater which is either not part of a drinking supply or has little permeability or storativity (State of Colorado 1992). Specific values for the cleanup levels were derived by analyzing values used by other states. The objective of the cleanup levels is that soil be clean enough so that drinking water standards are met in groundwater aquifers; the State may be lenient when this is either technically or economically not feasible. Groundwater monitoring is done to ascertain the contamination present in groundwater after remediation.

Delaware

Due to varied site conditions and geology in Delaware, state regulators advocate a site-by-site approach and have not derived any state-wide soil cleanup requirements for TPH or BTEX (Lerner 1993). Delaware places sites in one of three categories: A (high risk), B (moderate risk), or C (low risk). A site is considered high risk if groundwater is impacted, moderate risk if the property use is commercial, and low risk if the property use is industrial. There is a set of generic "screening levels" for TPH and BTEX which are applied to determine if remediation is necessary. These screening levels are usually prescribed cleanup levels for moderate risk sites. Low risk sites are generally cleaned up to background levels. High risk sites are cleaned up such that groundwater contamination does not exceed an MCL or detection limit. No modeling or quantitative methods are used to determine cleanup levels in this case; a quarterly groundwater monitoring program is implemented and remediation continues until groundwater goals are met and groundwater concentrations are stable for one year. In all three categories the State is very flexible in establishing cleanup goals. Generally, the responsible party hires a consultant and they and the State work together to negotiate exact cleanup goals which are feasible and protective of the environment.

Florida

Florida has developed a guidance level for soil TPH concentrations. Soils with TPH levels exceeding the guidance level be remediated. Florida does not have cleanup criteria for TPH and BTEX as such, but does apply standards for total recoverable petroleum hydrocarbons (TRPH) and total volatile organic aromatics (VOAs) (State of Florida 1992). The remediation goals for VOAs in soil are risk-based and are derived using a very conservative residential scenario which allows for soil ingestion by children (Conrardy 1993). The remediation level for TRPH in soil has the protection of groundwater as its purpose and is much less rigorously derived. This level is twice the groundwater TRPH standard, and is based on the conservative assumption that at most half of the soil contamination will leach into groundwater.

Georgia

Georgia is concerned with both groundwater and surface water (State of Georgia 1989). Stated cleanup standards apply only for a contaminant plume with a boundary within three miles of a public water withdrawal point, or within one-half mile of a nonpublic water withdrawal point. The levels are driven by Georgia's in-stream state water quality standards: soil concentrations less than required cleanup standards ensure that contaminants leaching from soil into surface water are in concentrations sufficiently small that state surface water standards are met. The specific levels were derived by combining knowledge of other states' regulatory approaches with an accepted background level of 100 ppm TPH for industrial sites and a conservative estimate that gasoline is at most 5% benzene, 5% toluene, 5% ethylbenzene, and 5% total xylenes (20% BTEX) (Gottschalk 1993).

Hawaii

In Hawaii, two sets of remediation goals exist for hydrocarbon spills based on their location relative to a "line" running around the perimeter of each Hawaiian island delineating drinking water (on the mountain side of the line) from non-drinking water (on the ocean side of the line) (Seid 1993.) For drinking water, a remediation goal based on the MCL is used; for non-drinking water, the remediation goals are based on water quality standards (acute and chronic criteria.) In both cases, the appropriate water standard is multiplied by a very conservative attenuation factor dependent on the contaminant's mobility and toxicity. This factor is 10 for all BTEX compounds but benzene; a factor of 1 is used for benzene. TPH is not regulated because no water quality standards exist for TPH. If the contaminant of concern is other than benzene, ethylbenzene, toluene, acenaphthene, fluoranthene, or naphthalene, the responsible party may opt for one of the following two alternatives in place of applying the cleanup standards described above: (1) perform a human health/ecological risk assessment using EPA Superfund guidelines to derive alternative cleanup criteria, or (2) implement a monitoring program, provided there is no exposure pathway.

Idaho

The ultimate goal of Idaho's remediation goals is to ensure that groundwater hydrocarbon concentrations meet federal standards (Wicherski 1993). Benzene drives the soil remediation goals because it is the most carcinogenic and the most mobile of the petroleum hydrocarbons. Thus, the prescribed BTEX and TPH levels for soil are the concentrations that will allow the groundwater concentration of benzene to remain below the MCL of 5 ppb. Exact numerical values for cleanup levels were selected after analysis of other states' levels. Oregon's regulatory approach was of particular importance.

Illinois

Illinois has formulated corrective action levels for BTEX using groundwater protection as the primary objective (Potter and Tin 1993). However, these levels apply only to USTs and not to above-ground spills. Regulators consider a site's soil type, soil permeability, and contribution of impacted groundwater to a water supply, and assign one of two sets of corrective action levels based on these criteria. Modeling and simulation techniques were used to calculate the two sets of corrective action levels. The levels are based on the concentrations of BTEX in soil which will not result in exceedance of existing state groundwater quality standards. The State of Illinois chooses to regulate hydrocarbon contamination using only a BTEX level; no TPH level has been developed.

Kansas

Kansas developed corrective action levels for TPH and benzene with the goal of protecting the state's groundwater. These levels are flexible; State regulators' professional judgment plays a significant role in determining which levels are actually applied (Sexton 1993). The TPH level was selected based on: the concentration where fumes are first noticeable; the concentration that can be easily detected by laboratory equipment; the concentration which exceeds background; TPH levels where leaching into groundwater occurs, and; the ability to quantify human health risk (Blackburn 1993). The benzene level is the concentration of benzene in soil which would result in a groundwater concentration of 0.07 ppm, assuming an attenuation factor of 20. The amount 0.07 ppm value was established as a "hazardous" quantity of benzene in groundwater many years ago by researchers developing the TCLP test. While more recent research indicates that this value could be increased, Kansas prefers to maintain the original value to assure the protection of human health and the environment.

Louisiana

Louisiana has no regulations or promulgated remediation goals for BTEX/TPH cleanups in soil (Mayeux 1993). Because of the state's diverse geology, each site must be considered individually. Typically, the responsible party hires a consultant to derive site-specific cleanup goals using techniques such as fate-and-transport computer simulation or human health risk assessment. The consultant meets with state regulators to propose the derived levels with appropriate scientific justification. The State accepts or rejects the proposal based on past experience cleaning up similar sites. Currently, Louisiana is formulating a risk-based computer model which will arrive at cleanup levels based on site-specific parameters. This model will not assume the role the consultants have always had; it will merely be used to give state regulators a set of site-specific cleanup objectives with which to compare the consultants' levels for a more objective assessment of the validity of the consultants' conclusions.

Maryland

Maryland's guidance level of 10 ppm TPH is based on best available technology for cleanup (Meade 1993). If contamination in excess of 10 ppm TPH is found, a site-specific risk characterization is performed to determine if remediation is warranted. Property use, groundwater usage, potential for contaminant migration, and human exposure pathways are considered when site-specific remediation goals are developed. The protection of groundwater is of primary importance. A groundwater monitoring program is implemented and remediation continues until groundwater contamination reaches asymptotic levels.

Massachusetts

Massachusetts' approach to regulating hydrocarbon contamination is almost identical to that of Oregon. The State has devised a numerical "matrix" of remediation goals for TPH by applying an attenuation factor to calculate soil concentrations which would result in groundwater contamination (Fitzgerald 1993; Locke 1993). Site characteristics, such as the frequency and intensity of human exposure to the contaminants of concern, accessibility of the contamination (*e.g.*, its depth below ground surface), and the potential of the contaminants to leach into the water table, are used to select the most relevant cleanup value from this matrix. Human health risk assessment equations and the fate-and-transport computer models SESOIL and AT123D were used to derive a range of cleanup levels for benzene, toluene, ethylbenzene, and total xylenes. If the responsible party can prove that the State's leachability assumptions used in deriving this matrix are overly conservative for the particular site in question, the State will permit the applicable cleanup level to be raised appropriately. The responsible party may also elect to perform a site-specific risk characterization and derive site-specific cleanup levels.

Michigan

The State of Michigan employs a combination of techniques to arrive at its corrective action levels for BTEX; TPH is not regulated (Howard 1992; MEPA 1993). The objective of these levels is to protect both groundwater quality and human health. Three methods exist for the derivation of site-specific levels: Methods A, B, and C.

Method A is the most conservative and requires the use of either a method detection limit or the background level of petroleum hydrocarbons present at the site as the cleanup level. Establishment of a background level involves taking soil samples in areas of the site which are not impacted by petroleum contamination and determining an "average" level of petroleum hydrocarbons present in the unimpacted areas. Method B is considered moderately conservative. Under Method B, risk-based (but not site-specific) soil cleanup levels are applied; these levels were derived using a residential land-use exposure scenario which incorporates ingestion of soil, dermal contact with soil, and the ingestion of groundwater. Method C is also a risk-based soil cleanup level, but is not developed with a residential scenario. Instead, the site is characterized and a site-specific exposure scenario is developed. This Method is typically used at industrial sites, where a residential scenario is not appropriate. If a risk-based value for a compound is calculated to be less than its method detection limit, the method detection limit is used as the cleanup level (Howard 1993).

Michigan allows the responsible party to select one of these three methods based on current and proposed land use, but state regulators reserve the right to object if they believe that an inappropriate method is chosen. Method B is most frequently chosen because it provides the most conservative estimate without excessive cost. Method C, while generally less conservative an estimate than B, is often cost-prohibitive because of the extensive site characterization required. To lower the cost of Method C, the State of Michigan is currently developing a generic industrial exposure scenario analogous to its residential exposure scenario.

Minnesota

Minnesota's remediation goals for surface spills are based on protection of both groundwater and public health (Aho 1993). State regulators work with the responsible party and their consultant to arrive at site-specific cleanup levels. The consultant may use a variety of techniques for developing the cleanup goals; groundwater modeling and informal human health risk assessment are commonly used. Often a groundwater monitoring program is implemented to ensure that the remediation's objectives have been met. The State is flexible in accepting site-specific cleanup requirements but insists upon a thorough analysis of the site. It is important to consider the use of the potentially affected aquifer (drinking water, potential drinking water, or other), the potential for vertical and horizontal migration, and the remediation cost. The goal of any cleanup levels is to ensure that both state drinking water standards and surface water standards are met. State drinking water standards are MCLs for public water supplies and values derived by the Minnesota Health Department for private wells. BTEX constituents are not usually monitored.

Missouri

Missouri's regulatory approach to soil cleanup levels BTEX and TPH is specifically for USTs (Schroeder 1993). Missouri regulators examined levels set by other states and selected an "average level" as their guidance level. Missouri applies a different set of soil cleanup levels for each of three soil types: excavated or remediated soil, undisturbed soil, and soil which has the potential to impact groundwater. Soil which may impact groundwater must be cleaned up to soil concentrations which ensure groundwater concentrations will be at or below a set of prescribed state groundwater levels. If the groundwater is potable, the state groundwater level for benzene is equal to the federal benzene MCL.

New Hampshire

New Hampshire's techniques for deriving soil remediation goals for TPH and BTEX are patterned after those of California (Lombardo 1993). The same groundwater models are used, but conditions specific to New Hampshire rather than California are used as input parameters. In the near future, New Hampshire will no longer regulate TPH concentrations in soil.

New Jersey

Three sets of guidance levels exist: for residential soil, non-residential soil, and soil which has the potential to impact to groundwater (Richter 1993) Land use determines whether a site is classified as residential or non-residential. The groundwater impact criteria are applied if the affected aquifer is classified as drinking water (as most aquifers in the state of New Jersey are), or is classified as an important natural resource by the State. If two sets of criteria are relevant, the most stringent one is applied. All three sets of guidance levels are risk-based, derived to be protective of human health. EPA policies and methodologies for human health risk assessment greatly influenced New Jersey's procedure for deriving these levels (State of New Jersey 1992).

New York

For concentrations of petroleum hydrocarbons in soil to be in compliance with New York State's guidance levels, groundwater, human health, and fish and wildlife must be protected, and nuisance characteristics (*e.g.*, odor, taste) must be eliminated (State of New York 1992.) Groundwater is considered protected if petroleum-contaminated soil is leaching contaminants in low enough concentrations such that groundwater standards are met. In order to determine these concentrations, the Toxicity Characteristic Leaching Procedure (TCLP) is used to simulate site-specific conditions and measure how much contaminant is capable of migrating into the water table. A cost-effective alternative to the TCLP is to measure the contaminant concentration in the soil and divide by 20 to calculate the maximum possible contaminant concentration which will leach into groundwater. Groundwater standards applied by the State of New York are the more stringent of either NYSDEC groundwater standards or NYSDOH drinking water standards. Human health is considered protected if contaminant concentrations in soil are less than Human Health Guidance Values (HHGV). HHGVs are derived from toxicity data contained in the Health Effects Assessment Summary Table (HEAST) Report using a soil ingestion scenario. If sediments are impacted, fish and wildlife are considered protected if the concentrations of hydrocarbons in sediment do not exceed New York State's Sediment Guidance Values. These values have not been derived for BTEX or TPH; only five PAH compounds have Sediment Guidance Values. Two different sets of levels have been developed: one set for gasoline, and another for fuel oil.

Ohio

Like many other states, Ohio has developed a matrix of remediation goals corresponding to varying site conditions (McClure 1993). Site conditions which play an important role in selecting values from the matrix are soil type, distance from drinking water source(s) or conduit(s), and proximity to utility lines. Sites are given a numerical score based on their attributes and the cleanup levels are selected from the matrix based on this score. Ohio used risk assessment procedures and principles of contaminant migration and attenuation to interpolate its matrix of remediation goals from "safe" soil contaminant levels derived by the Ohio EPA (Rowe 1993).

Oregon

Oregon has developed three sets of state soil cleanup standards corresponding to three levels of stringency. For each site, the State assigns a set based on the site's score from a numerical ranking procedure. Regulators evaluate the site and assign a numerical score in each of the following five areas: (1) depth to groundwater, (2) mean annual precipitation, (3) native soil or rock type and permeability, (4) contribution of the uppermost aquifer to a drinking water source, and (5) potential receptors, which are based on both the distance to the nearest well and the number of people at risk (Oregon 1990). A high potential impact to the water supply corresponds to a high score in each area; a high overall score warrants cleanup to a more stringent standard than if the score were low. If a score in any of the five areas cannot be ascertained, it is assigned the highest, most conservative possible score. The specific cleanup value for TPH was assigned assuming a dilution and attenuation factor of 100; the value for this factor was determined based on research conducted by EPA. Compound-specific cleanup levels for benzene, toluene, ethylbenzene, and total xylene were derived using EPA fate and transport computer models SESOIL and AT123D, and human health risk assessment procedures (Anderson 1993).

South Dakota

South Dakota set its soil remediation goals after examining other state's methods and cleanup levels (Miller 1993). State regulators selected the MCL for xylene to be the groundwater standard for TPH and established soil remediation goals which would ensure groundwater concentrations of TPH never exceed this level. The soil remediation goals cover a range of 10 to 100 ppm TPH. The lower bound of 10 ppm for TPH in soil was selected because the state groundwater quality standard for TPH is 10 ppm, and it was conservatively assumed that a 10 ppm concentration in soil would never result in a 10 ppm level in groundwater. The upper bound of 100 ppm TPH was based on levels used by other states. Regulators consider characteristics such as depth to groundwater, extent of vertical migration, and soil permeability when assigning a site-specific remediation goal within this range (State of South Dakota 1991). Remediation must result in a decrease in adverse aesthetic properties (appearance, smell) caused by the contamination.

Tennessee

Tennessee formulated state soil cleanup standards with the primary objective of protecting groundwater (Tennessee Department of Health and Environment 1989). According to regulations, cleanup levels for soil vary according to two site characteristics: soil permeability and whether or not the groundwater below the site contributes to a drinking water supply. The standards were developed using the EPA's derived attenuation factor of 100, combined with approaches used by other states, especially California (Head 1993). The responsible party may hire a consultant to derive site-specific standards and petition the State to apply these standards. The State may accept or reject the proposal, based on the adequacy of its defense. State regulators consider it important that the consultant include the following in the analysis: (1) physical/chemical characteristics of petroleum, including toxicity, persistence, and potential for migration, (2) hydrogeologic characteristics of the site, (3) proximity, quality, and current/future use(s) of the groundwater, (4) an exposure assessment, and (5) proximity, quality, and current/future use(s) of surface waters.

Texas

Texas has action levels for soil which, when exceeded, trigger a detailed site investigation. These action levels are based on soil grain size (Pena 1993). Upon completion of the site investigation, site-specific data are recorded on a questionnaire and used as input parameters for a site-specific risk assessment computer model developed by the American Petroleum Institute. The model yields site-specific soil cleanup levels for TPH and BTEX.

Utah

Utah formulated guidance levels after examination of the rationale of several other states, particularly Oregon and California (Stonestreet 1993). If TPH or BTEX are detected at concentrations above the guidance levels, a detailed site investigation is conducted. Specific remediation goals are developed during the course of this investigation; the responsible party may or may not hire a consultant to assist in their derivation. The goal of soil cleanup is to achieve groundwater contaminant levels which are below MCLs. Groundwater monitoring programs are essential in determining what type of remediation is necessary and when remediation goals have been met (Jenkins 1993).

Washington

Washington's remediation goals were established to protect the state's groundwater (Wilhelm 1993). Washington has three approaches: (A) use of a "standard" set of levels for commonly encountered substances which are based on federal standards and cleanup levels used by other states; (B) use of a site-specific risk-based estimate based on a residential exposure scenario, and (C) use of a site-specific risk-based estimate based on an industrial exposure scenario. Method A is intended for sites that are either small or have only a few contaminants, such that a risk assessment would be cost-prohibitive (State of Washington 1991). Under Method A, soil hydrocarbon concentrations must be reduced such that groundwater concentrations of TPH do not exceed 1000 ppb, groundwater concentrations of the four BTEX constituents do not exceed their MCLs, and any "adverse aesthetic qualities" such as smell and taste are reduced. Under Methods B and C, total lifetime cancer risk must be less than 1 in 100,000. Of the three Methods, Method B is most frequently used.

Wisconsin

Wisconsin uses action levels for TPH and BTEX to trigger a site investigation. These action levels are method detection limits. If cleanup is prescribed by the state, site-specific cleanup levels must be derived (McCurry 1993). The State works with the responsible party and a consultant to derive the cleanup levels. Several approaches are acceptable, including fate and transport modeling and use of detection limits or remediation techniques. The State is flexible when considering allowable levels. Their objective is to arrive at cleanup levels which are technically and economically feasible and restore the environment to its natural state prior to the contamination. If at all possible, the State requires soil be cleaned up to the point that state groundwater quality regulations are met.

GLOSSARY OF TERMS

absorption. The process whereby toxicants cross body membranes and enter the bloodstream.

additive effect. A situation in which the combined effect of two chemicals is equal to the sum of the effect of each agent given alone.

average daily dose (ADD). The average dose received on any given day during a period of exposure, expressed in mg/kg body weight-day. Ordinarily used in assessing noncarcinogenic risks.

antagonistic effect. A situation in which the combined effect of two chemicals is less than the sum of the effect of each agent given alone.

carcinogen. A chemical or physical agent that causes an increase in tumors in exposed organisms or individuals.

chronic exposure. A persistent, recurring, or long-term exposure, as distinguished from acute. Chronic exposure may result in health effects (such as cancer) that are delayed in onset, occurring long after exposure has ceased.

chronic toxicity. An adverse effect (*e.g.*, liver damage, cancer) resulting from long-term exposure to a chemical.

dose. The amount of a chemical received by the target organism (*e.g.*, humans) or a target organ (*i.e.*, delivered dose); it is generally reported in units of weight of the substance (*e.g.*, mg or micrograms) per body weight of an individual (*e.g.*, in kg) per unit time (*e.g.* hours or days).

dose-response assessment. The second step in the risk assessment process. This step describes the quantitative relationship between the amount of exposure to a chemical and the extent of toxic injury or disease. Data are derived from animal studies or, less frequently, from studies in exposed human populations. Many dose-response relationships can exist for a chemical agent, depending on conditions of exposure (*e.g.*, single versus repeated and prolonged exposures) and the type of response (*e.g.*, cancer, birth defects) being considered. This process is highly complex, taking into account diverse information about the body's ability to transform a chemical into more toxic metabolites up to a point where overload occurs, variations in sensitivity to doses of toxic substances, and differences between the mechanisms of toxicity in test organisms (*e.g.*, laboratory rodents) and in human target organs. In many cases, the features of a dose (*e.g.*, duration, frequency, and route) have a great impact on the degree of toxic potency. Specialized procedures must be employed to assure that later characterization of toxic risk is as scientifically defensible as possible.

epidemiology. The study of the association of human disease with environmental factors, such as chemical exposure.

exposure. The amount of material ingested, inhaled, or otherwise contacted by an organism; generally reported in concentration units such as ppm, ppb, mg/m^3, or in dose units of mg/kg-day.

exposure assessment. This is the third step of the risk assessment process. It describes the nature and size of the various populations exposed to a chemical agent, and the magnitude and duration of their exposures. The assessment might include current, and anticipated future exposures. This step also involves characterizing the nature of the populations likely to come into contact with the chemicals under evaluation. This includes determinations of not only the numbers of individuals potentially exposed, but also consideration of the distribution of age, gender, and unique conditions such as pregnancy, childhood, senescence, preexisting illness, and lifestyle.

exposure duration. The length of time an organism is in contact with a chemical.

exposure pathway. An exposure pathway describes a mechanism by which a population or individual can be exposed to chemicals present at or migrating from a site. An exposure pathway consists of the four following components:

- a source and mechanism of chemical release to the environment;
- an environmental transport medium for the released chemical;
- a point of potential human contact with the contaminated medium; and
- a human exposure route at the point of exposure.

exposure point. An exposure point is defined as the location of potential contact between a receptor population and a chemical of concern. The objective of determining exposure points is to identify specific locations where receptor populations may be potentially exposed to chemicals of concern contained within environmental transport media.

exposure route. An exposure route is defined as the mechanisms by which a chemical comes in contact with the receptor population, *e.g.*, ingestion or inhalation.

hazard identification. This is the first step in the risk assessment process. It is a determination of where there is a causal relationship between exposure to a chemical and an injurious effect on health. It involves gathering and evaluating toxicity data on the types of health injury or disease that may be produced by a chemical and on the conditions of exposure under which injury or disease is produced It may also involve characterization of the behavior of a chemical within the body and the interactions it undergoes with organs, cells, or even part of cells. Data of the latter types may be of values in answering the ultimate question of whether the forms of toxicity known to be produced by a chemical agent in one population group or in laboratory animals are also likely to be produced in the human population group of interest. Note that risk is not assessed at this stage; hazard identification is conducted to determine whether and to what degree it is scientifically correct to infer that toxic effects observed in one setting will occur in other settings (*e.g.*, are chemicals that are found to be carcinogenic or teratogenic at high doses in experimental animals also likely to be so in humans exposed to high - or even low - doses?).

hazard quotient (HQ). An indicator of the degree of hazard for noncarcinogenic effects resulting from exposure to a single chemical. The hazard quotients are added together to calculate a hazard index (HI) to examine exposure from multiple chemicals.

hematopoietic. Describing the formation of blood in the body.

gavage. The introduction of material into the stomach by means of a tube.

interspecies extrapolation. A method to apply the results of experimental studies in animals to humans: also called cross-species extrapolation.

intraspecies extrapolation. The differences within a species (*e.g.*, humans) that cause individuals to differ in susceptibility (and, thus, response) to a chemical or agent.

molecular weight. The sum of the atomic weights of all the atoms of a molecule.

no-observed-adverse-effect-level (NOAEL). A term used to describe the dose that elicits no toxicity in an animal bioassay or human study.

noncarcinogen. A chemical or physical agent that does not cause an increase in the tumor rate in exposed organisms or individuals.

nonthreshold effect. A response that is proportional to a level of exposure.

pharmacokinetic. The study of the absorption, metabolism, and action of drugs.

reference concentration (RfC). An estimate of daily exposure by inhalation (expressed as micrograms of substance per cubic meter of air per day) that is likely to be without appreciable risk of adverse noncarcinogenic health effects in the humans population over a lifetime; technically the NOAEL divided by the appropriate uncertainty or modifying factors.

reference dose (RfD). This is an estimate of a daily exposure by ingestion or dermal contact (expressed as milligrams of substance per kilogram of body weight per day) that is likely to be without appreciable risk of adverse noncarcinogenic health effects in the human population over a lifetime; technically the NOAEL divided by the appropriate uncertainty factors.

USEPA has developed various types of RfDs depending on:

- the exposure route (*i.e.*, oral or inhalation);
- the critical effect (*i.e.*, developmental or other); and,
- the length of exposure being evaluated (*i.e.*, chronic, subchronic or single event).

The USEPA defines a chronic RfD as an estimate of a daily exposure level for the human population that is unlikely to result in deleterious effects during a lifetime. These chronic RfDs are used to evaluate the potential noncarcinogenic effects associated with exposure periods between 7 years and a lifetime.

Subchronic RfDs have been developed by the USEPA to characterize potential noncarcinogenic effects associated with shorter term exposures (*i.e.*, periods between two weeks and seven years). Where only a chronic RfD has been developed by USEPA, a subchronic RfD has been estimated by multiplying the chronic RfD by 10. A factor of 10 is generally used by USEPA as the uncertainty factor applied to subchronic toxicity data to derive a chronic RfD (USEPA, 1989).

<u>risk assessment.</u> The characterization of the potential adverse health effects of human exposure to environmental hazards. The basic risk assessment paradigm is made up of four elements: hazard identification, dose-response assessment, exposure assessment, and risk characterization.

<u>risk characterization.</u> This is the fourth, and final, step of the risk assessment process. It involves integration of the data and analyses from the other three steps of risk assessment (hazard identification, dose-response assessment, and exposure assessment) to determine the likelihood that the human population of concern will experience any of the various forms of toxicity associated with a chemical under its known or anticipated conditions of exposure. This step includes estimations of risk for individuals and population groups, and a full exposition of the uncertainties associated with the conclusions. Scientific knowledge is usually incomplete, so that inferences about risk are inevitable. A well-constructed risk assessment relies on inferences that are most strongly supported by general scientific understanding, and does not include blanket conservative assumptions derived for use in the absence of actual data simply for ease of risk management or public policy directives.

<u>route-to-route extrapolation.</u> A method to apply the results of a study involving one route of administration of a chemical (*e.g.*, ingestion) to predict the results via another route of administration (*e.g.*, inhalation).

<u>synergistic effect.</u> A situation in which the combined effect of two chemicals is much greater than the sum of each chemical when given alone.

systemic toxicity. A toxic effect of a chemical beyond its point of exposure.

target organ. The organ or organs that are the major site of toxicity of a chemical.

teratogenicity. The ability of a substance to cause fetal malformations.

threshold. A critical level of exposure below which a response attributable to the specific agent is not possible.

uncertainty factors. These factors, applied to NOAELs in calculations of RfDs, are intended to account for specific types of uncertainty inherent in extrapolation from the available data, including variations in the sensitivity of individuals in a population, extrapolation from animal data to humans, limitations in exposure duration, and other limitations in the experimental data. The use of these safety factors increases the health-protectiveness of the RfD.

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