

Risk-Based Methodologies for Evaluating Petroleum Hydrocarbon Impacts at Oil and Natural Gas E&P Sites

Regulatory and Scientific Affairs Department

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EXECUTIVE SUMMARY

This manual presents a risk-based approach for the management of hydrocarbon-impacted soil at E&P sites that emphasizes the protection of human health. This risk-based approach was derived from the work of the Total Petroleum Hydrocarbon Criteria Working Group (TPH-CWG) as later modified by the Petroleum Environmental Research Forum (PERF) as part of PERF Project 97-08. It generates a risk-based screening level, or RBSL, for crude oil in soil that can be used as part of a Tier 1 risk evaluation. This RBSL is expressed in terms of TPH (total petroleum hydrocarbon) in soil and represents the soil TPH concentration that is protective of human health. RBSLs are calculated using exposure equations that are recognized by the U.S. Environmental Protection Agency as providing conservative estimates (i.e., lower than necessary for the protection of human health) of acceptable hydrocarbon concentrations in soil. The manual also presents results from the application of this risk-based approach to a typical E&P site. These results confirm that the TPH concentration of 10,000 mg/kg in soil that is often proposed as a regulatory criterion for E&P sites is protective of human health.

TPH RBSLS FOR COMPLEX MIXTURES OF PETROLEUM HYDROCARBONS

Tier 1 TPH RBSLs were determined for seventy crude oils based upon the potential occurrence of non-cancer health effects and typical exposure pathways that exist at E&P sites. Since residential exposure scenarios were not considered relevant to most E&P sites, the primary focus was on commercial and non-residential uses of the sites. With regards to these uses, the exposure pathways of most concern were direct contact with hydrocarbon-impacted soil (i.e., soil ingestion, inhalation of soil particles, and dermal contact).

The TPH RBSLs that were calculated for direct contact with soil that was impacted by this wide variety of crude oils ranged from 42,000 mg/kg (4.2% by weight) to 85,000 mg/kg (8.5% by weight) TPH. These values are significantly greater than the TPH concentration of 10,000 mg/kg that is often proposed as the regulatory criterion for E&P sites. The TPH RBSLs for selected E&P wastes were also determined for the same exposure scenario. These values were very similar to those for the crude oil, ranging from 52,000 mg/kg (5.2% by weight) to 100,000 mg/kg (10% by weight). These results suggest that the TPH RBSLs for crude oil should provide a reasonable criterion for managing wastes that are present in soils at E&P sites.

IMPACTS OF METALS, PAHs, AND BENZENE ON TPH RBSLs

The concentrations of both metals and PAHs in crude oil are not sufficiently high to require TPH RBSLs below those that were determined based upon non-cancer health effects. For example, the lowest (i.e., most restrictive) non-residential TPH RBSL for crude oil, based upon the concentrations of the seven carcinogenic PAHs that were identified in over 70 crude oils, was 170,000 mg/kg. This calculation was based upon the target risk level for cancer of 1 in 100,000 that is recommended by ASTM and used by many states. This target level is also the midpoint of the acceptable risk range set by the U.S. EPA for evaluating contaminated sites under Superfund. These results suggest that the routine analysis of carcinogenic PAHs and metals in soil at E&P sites is not necessary to ensure protection of human health.

The understanding of the impact of benzene on the management of E&P sites is continuing to evolve. Using the risk evaluation methods presented in this document, it has been determined that TPH RBSLs for complex hydrocarbon mixtures (e.g., crude oils or gas condensates) will be based on direct contact with soil as the limiting exposure pathway as long as the benzene concentration in the parent mixture is less than 300 mg/kg. Approximately one-third of the 69 crude oils that were tested as part of the PERF study (97-08) contained less than 300 mg/kg of benzene; all 14 of the gas condensates contained benzene at concentrations above 300 mg/kg. At benzene concentrations above this threshold, a simple, conservative Tier 1 analysis indicates that benzene controls the risk at the site, where the limiting exposure pathway is not direct contact with soil but leaching of the benzene from soil to groundwater. As such, the Tier 1 TPH RBSLs that are derived for groundwater protection purposes at an E&P site can be below 10,000 mg/kg when these concentrations of benzene are present. Alternatively, meeting separate benzene RBSLs may be appropriate in some cases.

It is important to note that the concentrations of benzene in hydrocarbon-impacted soil at E&P sites can be significantly less than its concentration in fresh crude oil. This is due largely to the natural processes of weathering, like volatilization. Also, following release from the soil in either the vadose or saturated zones, benzene can biodegrade, thereby reducing the potential exposure to any human receptors. Both of these processes have the net effect of increasing the acceptable TPH RBSL for crude oil in soil. The specific impact of these processes on the RBSL, however, requires an analysis of the site-specific conditions at a site.

USE OF CONVENTIONAL TPH ANALYSES FOR SITE MANAGEMENT

Based on the work that has been conducted to date on crude oils, it has been demonstrated that 10,000 mg/kg of TPH in soil at E&P sites is protective of human health effects. In fact, this concentration is extremely conservative as it is a factor of four below the lowest TPH RBSL that was calculated for non-residential sites. This observation, combined with the fact that the crude oils that were examined were representative of crude oils from around the world, suggests that measurements of bulk TPH using conventional analytical methods can be used to assess compliance at most, if not all, E&P sites.

In some circumstances, it may be necessary to confirm the concentration of benzene in the hydrocarbon mixture at an E&P site since this is the one constituent that has the potential to decrease the acceptable TPH RBSLs at an E&P site. However, the effect of benzene on TPH RBSLs at any given E&P site will depend heavily upon the site-specific conditions. For example, at a site where a crude oil that is rich in benzene (i.e., >300 mg benzene per kilogram of oil) was recently spilled and the groundwater table is near the ground surface, it may be prudent to analyze soil samples for the presence of benzene. On the other hand, if the only evidence of hydrocarbon contamination at an E&P site is weathered crude oil from historical spills, the analysis of benzene in the soil is probably not necessary. Similarly, analyses of benzene are probably not required if the fresh crude oil contains low concentrations of benzene or if the potential for biodegradation of the benzene in the subsurface environment is significant.

PART I

INTRODUCTION

PURPOSE OF MANUAL

Purpose of Document:

Describe recent advances in risk-based decision-making and their use in establishing clean-up concentrations for E&P sites based on measurements of bulk total petroleum hydrocarbon (TPH).

Several organizations are addressing the risk-based management of hydrocarbon-impacted media:

- *American Petroleum Institute (API)*
- *Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG)*
- *Petroleum Environmental Research Forum (PERF) and*
- *GRI (formerly the Gas Research Institute, currently, GTI)*

TPH: *Total petroleum hydrocarbons, or TPH, is a measure of the total concentration of hydrocarbons in a water or soil sample. Since the amount of hydrocarbon extracted from a sample depends upon the method that is used, TPH concentrations will vary with the analytical method that is selected.*

The day-to-day operations at oil and gas exploration and production (E&P) facilities may include regulated onsite disposal of oily wastes or the unintended release of petroleum hydrocarbons to site soils. The management of these hydrocarbon-impacted media has been the focus of a significant amount of recent research by several organizations including the American Petroleum Institute (API), the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG), the Petroleum Environmental Research Forum (PERF), GRI, and individual oil and gas companies.

The purpose of this manual is to describe how recent advances in risk-based decision making can be used for assessing waste management practices and establishing cleanup levels at E&P facilities based on measurements of bulk total petroleum hydrocarbon (TPH). Specifically, key concepts and study results are presented on the human health risk assessment of the bulk TPH and specific components of concern including benzene, polycyclic aromatic hydrocarbons (PAHs) and metals in crude oil-derived E&P wastes. These new applications can yield hydrocarbon concentrations that are less restrictive than the current regulatory criteria while still being protective of human health. Ecological risks associated with TPH and other chemicals of concern are not addressed in this document.

CONTENT AND ORGANIZATION OF MANUAL

This manual has been written in a question and answer format. Common technical and regulatory questions have been identified and grouped into the following categories:

- Risk-based decision making
- Characteristics of crude oils, condensates, and E&P wastes in contrast to those of refined products
- Calculation of risk and risk-based screening levels
- Application of risk-based methodologies to E&P sites in the United States and overseas

In addition to each of these major sections, there are appendices that discuss the regulatory status of E&P wastes (Appendix A); present the equations for the calculation of risk-based screening levels (Appendix B); and discuss the effect of hydrocarbon-saturated soil conditions on risk-based screening levels (Appendix C). Lastly, a list of references, a glossary, and a list of abbreviations can be found at the end of the document.

PART II

RISK-BASED DECISION MAKING

WHAT IS IT?

Risk-based decision-making is the process of making environmental management decisions based upon an assessment of the potential risks that chemicals at a site may pose to human health and the environment. The Environmental Protection Agency of the United States (U.S. EPA) has developed a general framework for health risk-based decision making and has established general guidelines for determining what constitutes *acceptable* risk. These guidelines can be used to determine when some type of action is required at a site.

The general framework for risk-based decision making was originally developed by the U.S. EPA, largely in response to the requirements of the Comprehensive Environmental Response and Contingency Liability Act of 1980 (CERCLA). A major goal of this framework is to make certain that management decisions for environmentally impacted sites provide an adequate level of protection for human health and the environment. As part of this framework, a health risk evaluation process was developed and the overall risk characterization is used to guide site management decisions.

The risk evaluation process, as originally set out by USEPA, involves four elements:

- Hazard identification
- Exposure assessment
- Toxicity (or dose-response) assessment
- Risk characterization

It is complete, comprehensive, and can be used to evaluate health risks at all types of contaminated sites. Although the process was developed for use at sites impacted by hazardous materials, in reality it is equally applicable to all types of sites, including oil and gas industry E&P sites.

WHY USE IT?

TRADITIONAL APPROACHES NOT BASED ON RISK

Historically, regulatory programs in the United States have established environmental management goals (i.e., clean-up levels) for chemicals of potential concern at specific sites based on:

Chapter Overview:

- Explains process of risk-based decision-making
- Introduces concept of a tiered decision-making framework
- Contrasts risk-based approaches to use of generic site clean-up goals
- Discusses situations that warrant use of tiered, risk-based analysis of sites

CERCLA:

Also known as Superfund

An assessment of risk requires knowledge of:

- The hazard
- The people who may come into contact with the hazard
- The routes by which exposure to the hazard can occur

$$\text{Risk} \propto \text{Hazard} * \text{Exposure} * \text{People}$$



RCRA Exemption and Risk-Based Management:

The risk-based decision-making process provides an operator with a means to choose the proper management and disposal options for wastes. However, an E&P operator may be found liable for clean-up actions under RCRA Sections 7002 and 7003 for releases of wastes that pose an imminent and substantial endangerment to human health and the environment. For more information about the regulatory status of E&P wastes, see Appendix A.

- Background (or naturally occurring) chemical concentrations (i.e., those typically found in unaffected areas)
- Analytical detection limits
- Concentrations that may be attainable if the most aggressive technologies were used for site remediation.

However, since none of these goals is directly tied to the actual risks posed by the chemicals of concern, there is no way to determine whether or not these goals actually protect human health and the environment.

TRADITIONAL APPROACHES MAY MISALLOCATE RESOURCES

There is no way to determine the cost/benefit associated with achieving the management goals listed above, since the benefit of the action cannot be determined. Without any knowledge of the benefit resulting from a given action, there is no way to prioritize actions to focus them on those problems where the greatest potential for risk reduction exists. This could conceivably result in a portion of the public being left at risk, and in the misallocation of both the technical and financial resources of this country. This represents a problem because there is a limit to the resources that the United States has available to solve the environmental problems in the oil and gas, or any other, industry.

RISK-BASED APPROACHES PERMIT COST-BENEFIT ANALYSES

In contrast, risk-based approaches to site management clearly describe the potential health benefits that might result from a particular environmental management decision. Consequently, the actions that are taken at a site can be evaluated and prioritized based on the actual reduction in risk that would be achieved and technical and financial resources can be allocated appropriately.

SHOULD IT BE USED AT ALL SITES?

Like all technical methodologies and protocols, risk-based decision-making is not necessarily applicable to every situation at every E&P site. For example, there may be instances where a risk-based assessment concludes that TPH concentrations at a specific site do not pose a health risk. However, these same concentrations may produce unsightly conditions that may influence site management decisions.

It is also important to think carefully about the assumptions that are made when using risk-based decision-making for site management. Since it is not uncommon to have limited data available to conduct a risk-based evaluation of a site, there is generally a need to make some

basic assumptions in the analysis. Examples of assumptions include the toxicity of the materials in question or the duration and extent of potential exposures. In every analysis, it is important that the sensitivity of the risk-based decisions to the assumptions used be understood to determine how robust the analysis is and the circumstances that might justify the use of different assumptions. The greatest criticism of risk-based site management is that it can be manipulated to produce any result that is desired by the user. The primary defense to this criticism is to make certain that the analysis is completely transparent, to fully justify the assumptions that are made, and to examine the sensitivity of the outcome to the more critical of these assumptions.

WHAT ARE TIERED RISK-BASED DECISION-MAKING FRAMEWORKS?

One drawback of the risk-based decision-making process, as originally developed by U.S. EPA, is that it can require a substantial investment of technical and financial resources, as well as time. Also, the data required to complete the risk evaluation are often not readily available. For these reasons, tiered strategies tailored for specific types of sites have recently been developed by regulatory agencies and by independent organizations to permit its cost-effective use. One example of this type of effort is that developed by the American Society for Testing and Materials (ASTM).

The first significant risk-based decision-making development by ASTM was the *Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites*, ASTM #1739-95. The development of this guide was driven by the need to cost-effectively and expeditiously manage underground storage tank sites. The guide was finalized in 1995 and it has since been recognized by the U.S. EPA and used by many state regulators to revise UST (Underground Storage Tank) programs. ASTM completed a second guide in April 2000 with the development of the *Standard Guide for Risk-Based Corrective Action (E2081-00)*. This effort expanded the previous standard by facilitating the use of risk-based corrective action in Federal and state regulatory programs including voluntary clean-up programs, brown-fields redevelopment, Superfund, and RCRA corrective action.

In addition to these national efforts by ASTM, several state environmental regulatory agencies have also initiated unified risk-based corrective action programs that include voluntary, Superfund, and RCRA corrective action programs. Examples of these programs are the Massachusetts Contingency Plan, the Tiered Assessment Corrective Action Objectives of Illinois, Louisiana Department of Environmental Quality Risk Evaluation/Corrective Action Program, and the Risk Reduction Program of Texas.

Tiered Approach:

- **Tier 1 — Generic Screening Levels:** Compare chemical concentrations at site to generic, pre-determined clean-up goals.
- **Tier 2/3 — Site-Specific Target Levels:** Require more sophisticated site-specific data and analysis to yield less conservative clean-up goals. Increased assessment costs may be balanced by reduction in remediation costs.

All tiers are equally protective of human health and the environment.

Tiered risk-based frameworks led by ASTM:

- *Petroleum release sites (1995)*
- *Chemical release sites (2000)*

Several states now have unified risk-based corrective action programs.

Tiered approaches generally start with an initial screening stage, Tier 1, that uses a basic set of site assessment data and involves a comparison of the concentrations of chemicals in the different environmental media to predetermined risk-based screening levels. These Tier 1 risk-based screening levels are predetermined for different exposure pathways and different land uses. A site conceptual model is then used to determine the exposure pathways that may be present at a site for a given land use. If site concentrations are below the risk-based screening levels for each exposure pathway, the conclusion is drawn that chemicals of potential concern do not pose a significant risk to human health or the environment and that no remedial action is necessary. If site concentrations exceed Tier 1 levels, the site manager generally has the option of remediating the site to Tier 1 levels or alternatively, progressing to a more data and labor intensive Tier 2 or even Tier 3 analysis.

Tier 2 and Tier 3 analyses generally require increasingly sophisticated levels of data collection and analysis, which in turn result in increased costs. The trade-off for these increased costs will generally lie in lower remediation and overall project costs, because the clean-up goals defined by a Tier 2 or 3 analysis are likely to be higher than Tier 1 levels, and thus less costly to achieve. The clean-up goals of the Tier 2 and 3 analyses are generally higher than the Tier 1 analysis because the generic assumptions used in the Tier 1 levels are replaced with more relevant site-specific assumptions or data. They are not higher because they are less protective of human health or the environment. In fact, all three tiers of risk analysis provide an equal level of health protection.

Upon completion of each tier, the site manager reviews the results and recommendations, and decides if the cost of conducting the additional site-specific analyses is warranted. Using the tiered approach, an E&P site manager has the flexibility to forego the detailed risk characterization effort of a site-specific Tier 2 or 3 analysis and proceed directly to site actions that generally involve meeting conservatively low, generic site clean-up goals. In some cases, this approach may be the more cost-effective and more prudent management decision.

WHEN IS IT APPROPRIATE TO USE A TIERED APPROACH?

The decision to use the tiered risk-based strategies for site management is usually dictated by the nature of the site contamination and the complexity of the site conditions; however, it may also be dictated by the governing regulatory body.

At most E&P sites, it is likely that a tiered risk-based strategy will be the approach of choice. This is because E&P sites generally involve a known and very limited number of chemicals of potential concern (e.g., crude oil, gas condensates, selected additives), and they have relatively small operational footprints. Consequently, the lower tiers of risk analysis will often provide the most cost-effective site management approach.

Tiered risk-based strategies are appropriate for E&P sites since these sites:

- *Involve known and very limited number of chemicals*
- *Have relatively small operational footprints*

WHAT IS THE ROLE OF GENERIC SITE CLEANUP CRITERIA IN THE RISK-BASED DECISION-MAKING PROCESS?

Both generic and site-specific criteria have a potential role in the management of E&P sites. Generic site clean-up criteria, many of which are not explicitly risk-based, can be used as Tier 1 screening level criteria. E&P site managers can use these criteria for site management if the desire or need to generate a site-specific risk-based criteria is not present. For example, if a site in its current condition was already below the generic site clean-up criteria, there would be no need to incur the expense or spend the time to determine what the site-specific risk-based criteria would be. Similarly, for a given site, if the volume of impacted soil (or other environmental media) that exceeds the generic criteria is small, it may be more cost-effective to take the necessary remedial action to meet the generic criteria than to determine if the remedial action is really necessary by generating site-specific criteria. However, it should be recognized that those generic criteria that are not risk-based may or may not be protective of human health and the environment. One of the goals of the recent PERF research initiatives (i.e., PERF Project 97-08) was to derive a generic risk-based screening criteria against which existing, non risk-based criteria that are currently used for E&P site management could be compared.

Examples of generic site clean-up criteria for TPH in soils at E&P sites in North America (mg/kg)

- *Colorado:*
 - ◆ *1,000 (sensitive site)*
 - ◆ *10,000 (non-sensitive site)*
- *Louisiana: 10,000*
- *New Mexico: 100; 1,000; or 5,000*
- *Texas: 10,000*
- *Wyoming: 1,000 to 10,000*
- *Alberta (Canada): 1,000*

TIER 1 VERSUS TIER 2 OR TIER 3?

The development of tiered approaches for the risk-based analysis of sites was based on the premise that there are situations where conducting a detailed risk analysis may require more effort and time than immediate implementation of site remedial actions. For this reason, after every tier of risk analysis, the site manager must perform a cost/benefit evaluation to determine if it makes sense to proceed to the next level of risk analysis. Only if a clear benefit exists would the decision to move forward be made. For example, because the Tier 1 assessment is often based upon conservatively low, generic site clean-up goals, the extent of a site remedial action may be larger (and more expensive) than might be required if a more detailed site-specific Tier 2 analysis were conducted. However, additional time and expense will be incurred to complete the Tier 2 analysis. At this point, the site

Cost-benefit analysis will determine if the more detailed Tier 2 or Tier 3 analysis is warranted. Timing is also likely to be an important factor.

manager must evaluate the potential reduction in site remedial costs that may be realized by conducting the Tier 2 analysis and compare that reduction to the additional cost of conducting the risk analysis. If the potential savings outweigh the potential cost, it would be in the manager's best interest to move forward with the analysis. In some cases, it is not the cost that drives the decision but the schedule. If the time required to conduct the next tier of risk analysis is not acceptable to regulatory agencies or the public, then the decision to proceed with site remediation is essentially made for the site manager.

PART III

CHARACTERISTICS OF CRUDE OILS, REFINED PETROLEUM PRODUCTS, CONDENSATES, AND E&P WASTES

An understanding of the chemical, physical, and toxicological characteristics of crude oils, refined petroleum products, condensates, and E&P wastes is required for the effective application of risk-based decision-making. However, most of the available analyses of these materials will not support a rigorous assessment of risk. Several recent studies have improved this situation by providing the necessary data to support risk analyses [TPHCWG, 1999; Kerr, et al., 1999a; Kerr, et al., 1999b; Magaw, et al., 1999a; Magaw, et al., 1999b; McMillen, et al., 1999a; McMillen, et al., 1999b]. A summary of these chemical, physical, and toxicological data is presented here.

CHEMICAL CHARACTERISTICS

WHAT ARE THE CHEMICAL CHARACTERISTICS OF CRUDE OIL AND ITS REFINED PRODUCTS?

In the broadest sense, petroleum hydrocarbons can be divided into two classes of chemicals, saturates and unsaturates. The saturates, also referred to as alkanes or paraffins-, are comprised of three main subclasses based on the structure of their molecules: either straight chains, branched chains, or cyclic. Straight-chain compounds are known as normal alkanes (or n-alkanes). The branched chain compounds are designated isoalkanes and the cyclic compounds, cycloalkanes. [Petroleum geologists typically refer to alkanes as paraffins and cycloalkanes as cycloparaffins or naphthenes]. Within the unsaturates, there are two main subclasses, aromatics and olefins. This classification of petroleum hydrocarbons is summarized in Figure 1. The compounds encompassed by the classification, aliphatic hydrocarbons, include all of the non-aromatic compounds shown at the bottom of Figure 1 (i.e., n-alkanes, isoalkanes, cycloalkanes or naphthenes, and olefins). Aromatic hydrocarbons are comprised of one or more unsaturated cyclic structures, or rings. Benzene contains one such ring, while polycyclic aromatic hydrocarbons contain two or more rings (e.g., phenanthrene has three unsaturated rings).

Crude Oil

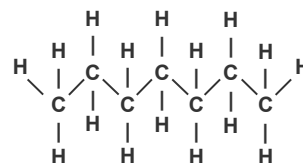
Figure 2 describes the major classes of petroleum hydrocarbons that are present in crude oil. The primary saturated and unsaturated hydrocarbons consist of n-alkanes, isoalkanes, cycloalkanes, and the mono-,

Chapter Overview:

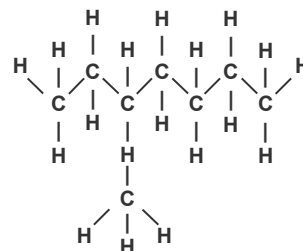
- Presents chemical, physical and toxicological characteristics
- Compares and contrasts characteristics of different materials

Saturates: (alkanes or paraffins)

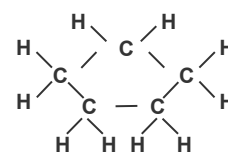
n-Alkane:



Isoalkane:

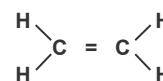


Cycloalkane:

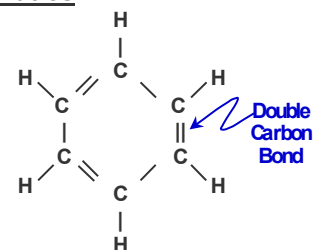


Unsaturates:

Olefins:



Aromatics:



Crude oil is composed almost entirely (i.e., 93% to >99%) of hydrogen and carbon, in the ratio of approximately 2:1. These elements form the hydrocarbon compounds that are the backbone of crude oil. Minor elements such as sulfur, nitrogen, and oxygen constitute less than 1 percent, to as much as 7 percent, of some crude oils. These elements are found in the non-hydrocarbon compounds known as asphaltene and resins.

di-, and tri-aromatics; there are no olefins in crude oil. In addition to these saturated and unsaturated hydrocarbons, there are also two non-hydrocarbon fractions (i.e., fractions that contain compounds in addition to carbon and hydrogen such as nitrogen, sulfur, and oxygen). These non-hydrocarbon fractions are the asphaltene and resins.

FIGURE 1. CHEMICAL CLASSIFICATION OF PETROLEUM HYDROCARBONS

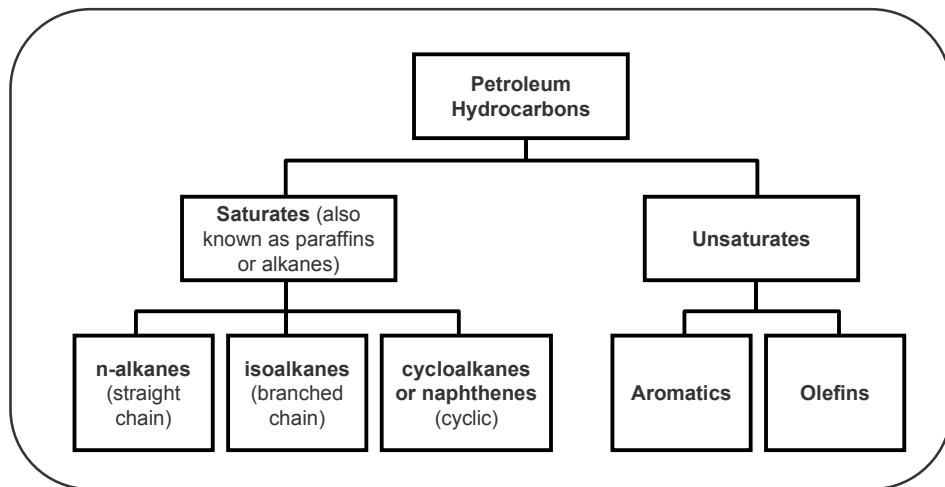
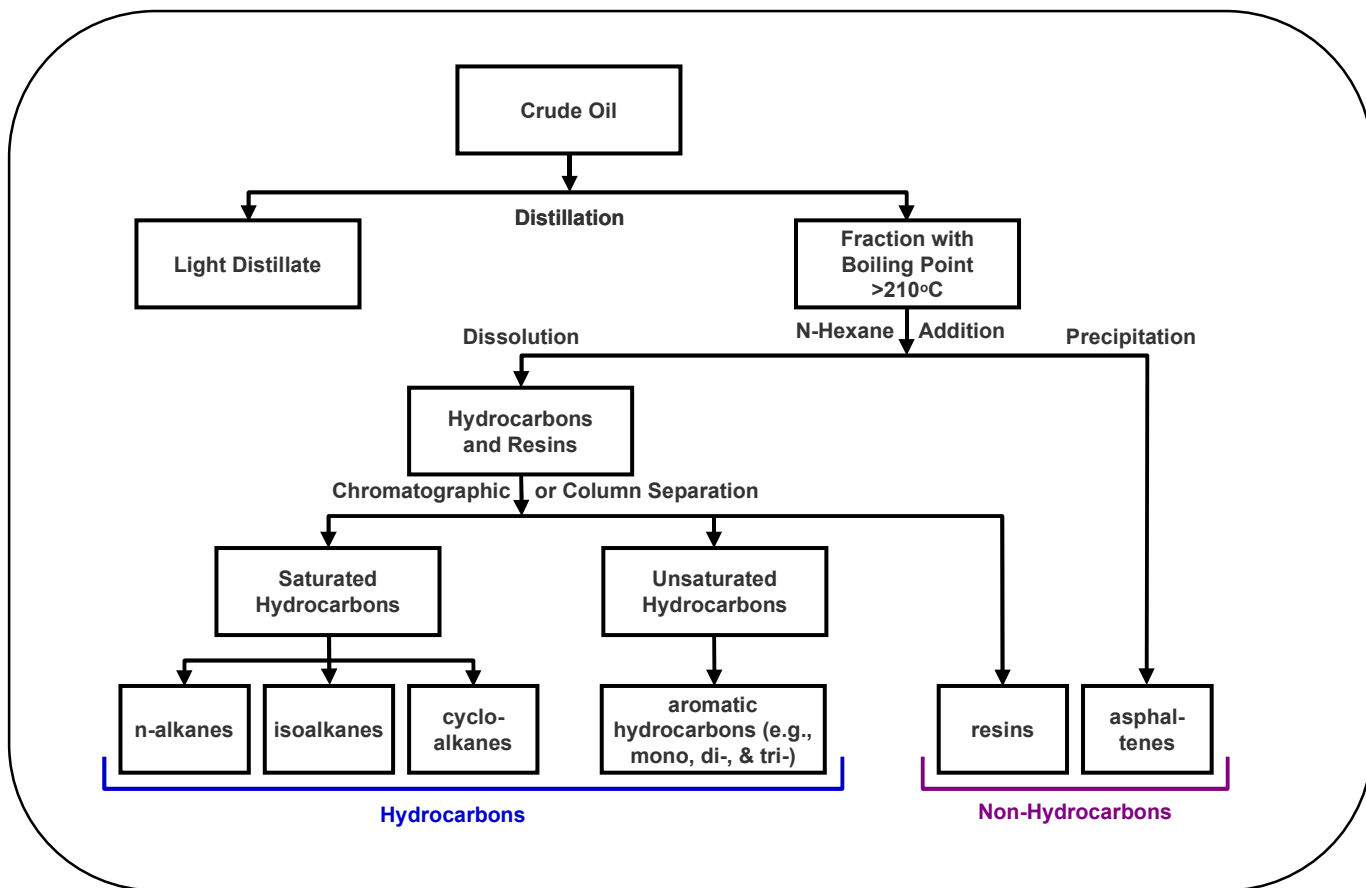


FIGURE 2. MAIN GROUPS OF CHEMICAL COMPOUNDS IN CRUDE OIL



The composition of 636 crude oils from around the world have been compared by Tissot and Welte [1978]. An examination of these data reveals that the proportions of saturates, aromatics, resins, and asphaltenes can vary dramatically, with the majority of normal crude oils lying within a composition envelope that is bounded in the following manner:

- 40 to 80% saturates
- 15 to 40% aromatics
- 0 to 20% resins and asphaltenes

Within these classes of hydrocarbons are compounds that have anywhere from 1 to more than 45 carbons in their chemical structure. The percentages of these compounds that are present vary among the different crude oils. An illustration of the differences in composition for two crude oils can be seen in Figure 3. Gas chromatograms give an indication of the carbon number range and hydrocarbon type (saturates versus aromatics) for the total petroleum hydrocarbons within a complex mixture. In this figure, the Widuri crude from Sumatra is dominated by normal alkanes or paraffins that produce a "picket fence" type pattern in the chromatograph which is typical of waxy crude oils. On the other hand, the SJV crude oil from California is dominated by a "hump" or unresolved complex mixture of hydrocarbons that are difficult for a gas chromatograph to separate. This "hump" is indicative of the prior biodegradation of hydrocarbons that occurred in the oil reservoir and is a common characteristic for many heavy crude oils.

Additional composition data for PAHs and heavy metals in crude oil are also presented in other recent references. Specifically, the concentration of the 16 priority pollutant PAHs and 18 heavy metals has been reported for a number of crude oils [Magaw, et al., 1999a; Magaw, et al., 1999b; Kerr, et al., 1999a; Kerr, et al., 1999b]. The analysis of PAHs in 60 crude oils revealed that the mean concentrations of seven carcinogenic PAHs were quite low for six of the seven compounds, ranging from 0.06 (indeno(1,2,3-cd)pyrene) to 5.5 (benz(a)anthracene) mg/kg oil. The mean concentration for chrysene was 28.5 mg/kg oil. Naphthalene accounted for as much as 85% of the total PAHs detected. For the metals analyses of 26 crude oils, the mean concentrations detected were less than 1.5 mg/kg of oil for all metals except nickel, vanadium, and zinc. The mean concentrations of these three metals were 20, 63, and 3 mg/kg of oil, respectively.

Refined Products

Since crude oil is comprised primarily of highly complex mixtures of hydrocarbons, it follows that the products refined from crude oil are also complex hydrocarbon mixtures. Indeed, they are even more enriched in hydrocarbons than crude oil since the refining processes

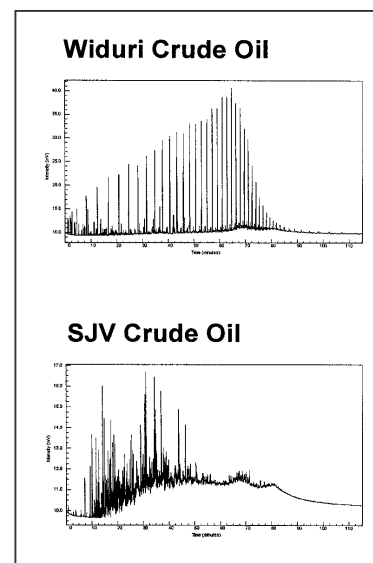
Composition of normal crude oil is bounded as follows:

- 40 to 80% saturates
- 15 to 40% aromatics
- 0 to 20% resins and asphaltenes

Carbon-Number Range:

Hydrocarbon mixtures are often defined in terms of the range of the number of carbons that are present in the individual compounds that make up the mixture. For example, gasoline is comprised of hydrocarbons that have anywhere from four to ten carbons in their chemical structure. As such, the carbon-number range for gasoline is C₅-C₁₀.

FIGURE 3. GAS CHROMATOGRAMS FOR TWO CRUDE OILS



Range of concentrations for carcinogenic PAHs and metals in crude oils (mean concentrations, mg/kg):

- Carcinogenic PAHs: 0.06 for indeno(1,2,3-cd)pyrene to 28.5 chrysene
- Metals: <1.5 except for nickel (20), vanadium (63), and zinc (3)

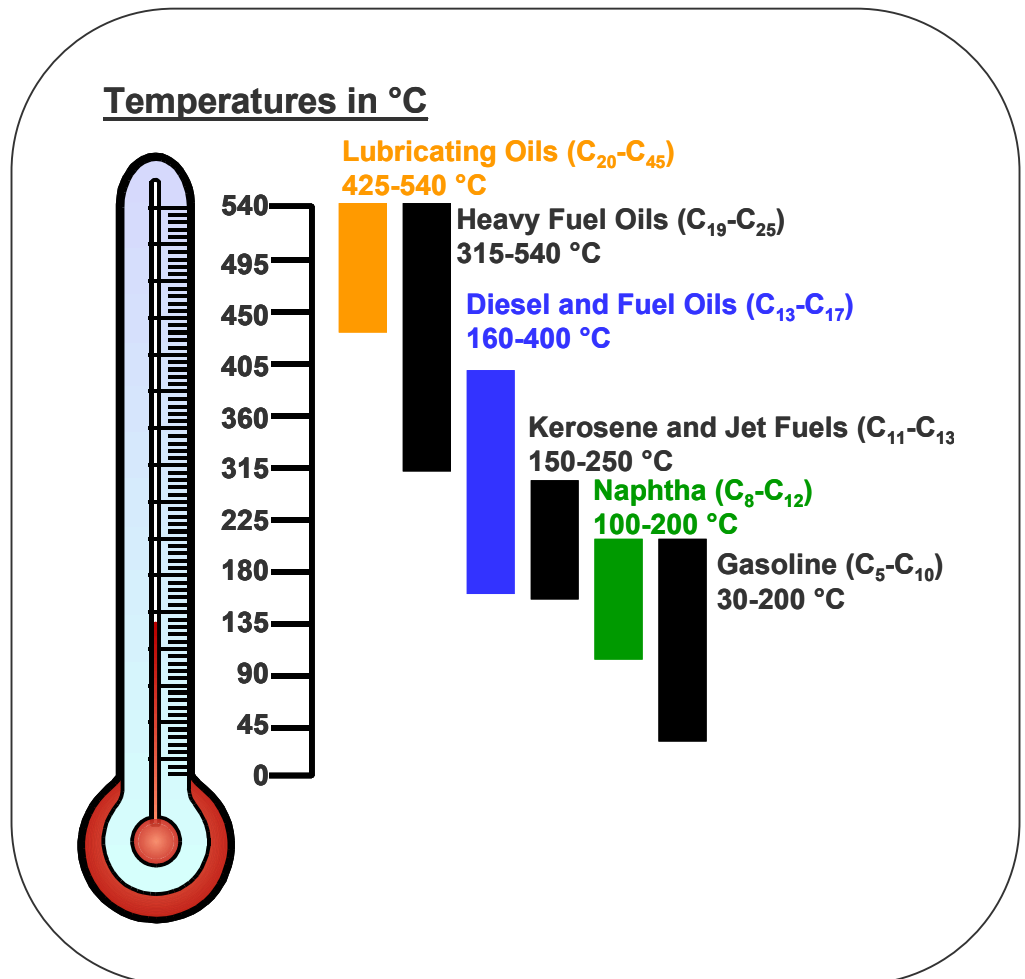
Blending agents and additives are also added to refined products. Examples of these include:

- Anti-knock agents (methyl-tert-butylether)
- Anti-oxidants (aminophenols)
- Metal activators (amino propane)
- Lead scavengers (ethylene dibromide)
- Anti-rust agents (sulfo-nates)
- Anti-icing agents (alcohols)
- Detergents (amides)
- Ignition improvers (nitrates)
- Combustion catalysts (M_nO , M_gO)
- Cold flow improvers (poly-olefins)

The addition of these materials and the amounts used vary substantially on a seasonal or regional basis throughout the United States.

used for their production either destroys nearly all of the non-hydrocarbons (i.e., asphaltenes and resins) or concentrates them in other products. Since it is extremely difficult to identify all the components of crude oils and its refined products, these materials are often characterized in terms of boiling range and approximate carbon number ranges as previously discussed. To illustrate this point, Figure 4 shows boiling points and carbon number ranges for six common crude oil products [ASTM, 1989]. Note that the carbon number ranges for the refined products are much narrower than that of the crude oil itself. Note also that the boiling points of the products increase as their carbon number range increases.

FIGURE 4. BOILING POINT AND CARBON NUMBER RANGES FOR SIX COMMON CRUDE OIL PRODUCTS



Blending agents and additives are also added to refined products. The nature and quantity of these materials that are added vary substantially on a regional basis throughout the United States.

WHAT ARE THE CHEMICAL CHARACTERISTICS OF CONDENSATES?

Gas condensates are extracted with natural gas in a liquid form. They have a narrower carbon number range than crude oil, typically extending from $<C_6$ to C_{30} .

Gas chromatograms of the saturated and aromatic hydrocarbon fractions of two condensates are shown in Figure 5. These fingerprints illustrate the large degree of variability that can exist for these hydrocarbon mixtures. In particular, it is clear that Condensate A encompasses a much broader range of hydrocarbons than does Condensate B. Also, the ratio of the saturated hydrocarbons to the aromatic hydrocarbons is quite different for these two condensates, increasing from 3.2 for condensate B to 5.8 for Condensate A.

The chemical composition of fourteen gas condensates was determined by the Petroleum Environmental Research Forum and GRI [Hawthorne, et al., 1998; Rixey, 1999]. From these studies, the following generalizations regarding the detailed chemical composition of the condensates can be made:

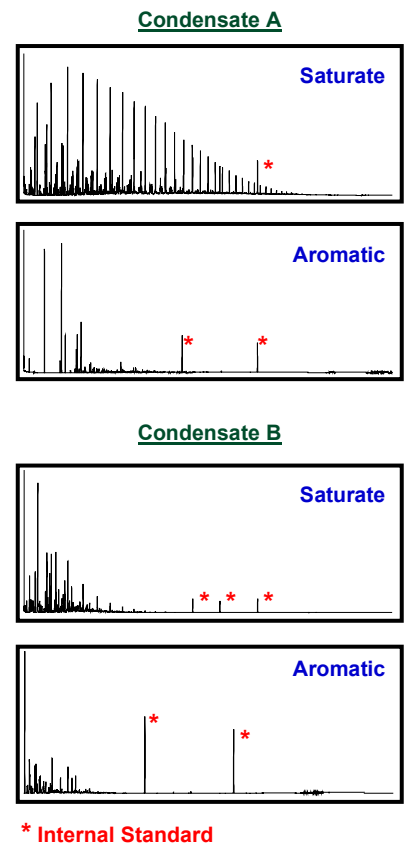
- Major chemical components are the straight-chained and branched saturated and unsaturated hydrocarbons.
- Benzene concentrations ranged from approximately 0.15 to 3.6% by weight.
- Only three of the seven carcinogenic PAHs were detected in condensates (benzo(b)fluoranthene, chrysene, and benzo(a)-anthracene). The highest mean concentration was that of chrysene, 1.8 mg/kg oil. The concentrations of the 16 priority pollutant PAHs ranged from 200 to 6,000 mg/kg oil, with more than 95 percent of the total being naphthalene.

From a somewhat broader perspective, the carbon number ranges that were represented by the condensates varied from a minimum range of C_5 to C_9 to a maximum range of C_6 to C_{30} .

WHAT ARE THE CHEMICAL CHARACTERISTICS OF E&P WASTES?

There are a variety of wastes that are generated during each step of the oil and gas exploration and production process. An extensive listing of these wastes is provided in a publication by the American Petroleum Institute, *Environmental Guidance Document: Waste Management in Exploration and Production Operations* [American Petroleum Institute, 1997]. These listings are tabulated based upon the specific phase of exploration and production operations which include: (1) exploration, (2) drilling, (3) well completion and workover, (4) field production, and (5) gas plant (including gas gathering) operations. A summary of the primary wastes that are identified with each operation is provided in Appendix A.

FIGURE 5. GAS CHROMATOGRAMS OF GAS CONDENSATES



* Internal Standard

Typical Characteristics of Condensates:

- Typical carbon number ranges: (1) Minimum: C_5 to C_9 and (2) Maximum: C_6 to C_{30}
- Benzene concentrations ranging from 0.15 to 3.6%
- Only three of seven carcinogenic PAHs (benzo(b)-fluoranthene, chrysene, and benzo(c)anthracene) were detected in condensates with chrysene having the highest mean concentration of 1.8 mg/kg oil.
- Total priority pollutant PAH concentrations: 200 to 6000 mg/kg (mostly naphthalene)

Appendix A provides a discussion of RCRA exemption for E&P wastes and definition of "associated wastes."

API and GRI conducted studies to characterize "associated wastes" from wellhead production operations:

- API analyzed 12 wastes; GRI, 20 wastes. Five common waste types were analyzed by both organizations.
- Wastes were characterized for:
 - (1) VOCs
 - (2) Semi-volatile organic compounds
 - (3) Trace metals

Hydrocarbons Detected in E&P Wastes:

- VOCs: benzene, carbon disulfide, ethylbenzene, toluene, and xylene
- Semi-volatile Organic Compounds: phenol, naphthalene, methyl-naphthalene, methylphenol, chrysene, and phenanthrene

The wastes that are uniquely associated with exploration and production operations are currently exempt from regulation under the Resource Conservation and Recovery Act (RCRA) as "hazardous wastes." Produced water and drilling muds are the two wastes that are produced in the largest volumes. RCRA-exempt "associated wastes" include hydrocarbon-containing wastes such as soil impacted with crude oil, tank bottoms, and workover fluids. Other potentially significant associated wastes include the gas processing fluids that are used to dehydrate and remove sulfur from the gas (i.e., glycols and amines) as well as used exploration additives such as biocides, frac fluids, and drilling fluids. [See Appendix A for a discussion of the RCRA E&P regulatory determination and definition of "associated wastes"].

Characterization Studies

Both API and GRI have conducted studies to characterize several of the associated wastes of oil and gas exploration and production. The API study [American Petroleum Institute, 1996] focused primarily on the characterization of the associated wastes from wellhead oil production operations. Complementing this effort, the GRI study [Gas Research Institute, 1993] emphasized the characterization of wastes from natural gas production associated with mainline compression/transmission, underground storage, and gas processing and conditioning. A common set of four samples from a single gas processing and conditioning facility were characterized in both studies.

The API study analyzed a total of twelve different associated wastes from oil and exploration and production sites. These wastes included:

- Tank bottoms
- Crude oil impacted soil
- Workover fluids (flowback from spent stimulation fluids)
- Produced sand
- Dehydration and sweetening materials (i.e., glycol waste, dehydration condensate water, spent molecular sieve, spent iron sponge, and used amine solutions)
- Pit and sump samples
- Rig wash waters
- Pipeline pigging materials

All but five of the wastes were characterized for volatile organic compounds (EPA Appendix IX of 40 CFR, Part 264: This Appendix of the Code of Federal Register presents a list of chemicals for groundwater monitoring at RCRA hazardous waste facilities. This list has also been

used in many other regulations including those associated with the land disposal of hazardous waste), semi-volatile organic compounds, and trace metals; the other five wastes (i.e., dehydration condensate water, spent molecular sieve, used amine solutions, rig wash waters, and pipeline pigging materials) were only characterized for volatile organic compounds.

GRI characterized a total of 20 different waste streams. Only five of these wastes overlapped with those that were characterized by API. These common wastes included spent molecular sieve, dehydration condensate water, pipeline pigging materials, tank bottoms, and glycol wastes. GRI analyzed their waste streams for volatile organic compounds, semi-volatile organic compounds, and trace metals.

Characterization Results

While the waste samples of the API and GRI studies were analyzed for a broad range of contaminants, very few of them were present above the analytical detection limits. More specifically, the findings of the studies can be summarized as follows:

- **Volatile Organic Compounds:** Only five of the Appendix IX compounds were detected by API in a total of 120 samples of the twelve waste categories. These compounds were benzene, carbon disulfide, ethylbenzene, toluene, and xylene. The GRI results mirrored these results as benzene, toluene, and xylene were the primary volatile organic chemicals that were detected. [Acetone and methylene chloride were also detected but their presence was attributed to cross contamination in the laboratory].
- **Semi-Volatile Organic Compounds:** API examined a total of 31 samples of eight waste categories for these compounds. The only chemicals that were detected were 1-methyl naphthalene, chrysene, and phenanthrene. Phenol, naphthalene, methyl phenols, and methyl naphthalenes were the only semi-volatile compounds that were detected by GRI.
- **Metals:** API detected a total of sixteen metals in 33 samples of eight waste categories. Of these detections, only two (i.e., arsenic and lead) exceeded the risk-based criteria that were previously established by API for soil/waste mixtures. The metals that were detected by GRI included arsenic, boron, barium, calcium, cobalt, chromium, copper, potassium, iron, mercury, magnesium, manganese, nickel, lead, and zinc.

Presence of hydrocarbons and trace metals in E&P wastes depend upon:

- *Nature of crude oil and unprocessed natural gas*
- *Location of oil or gas*
- *Type of natural gas processing*
- *Extent of biodegradation*

However, elevated concentrations of metals can also be attributed to other sources (e.g., pipe dope).

The above results are consistent with what would be expected given the inherent nature of crude oil and natural gas, where they are found, and the type of natural gas processing that is done. For example, it is well

known that volatile organic compounds are present in crude oil and unprocessed natural gas. Consequently, it is not surprising to find a subset of these compounds in exploration and production wastes. However, the specific concentrations of these chemicals that will be present depend on the characteristics of the crude oil and unprocessed natural gas that is extracted as well as the characteristics of the wastes. Similarly, it is known that crude oil and unprocessed natural gas contain trace amounts of the semi-volatile compounds and that these compounds might be detected in the associated wastes.

Lastly, since crude oil and unprocessed natural gas are produced from geological formations within the earth, it is expected that the metals that are contained within the earth's minerals would be present in both of them in varying concentrations. It is also expected that the associated wastes would contain detectable concentrations of these same metals, depending upon the characteristics of the geologic formation and the drilling and producing practices that were used. However, in many instances, it is the presence of other metal sources such as pipe dope that leads to elevated concentrations in the associated wastes. [The API study cautioned that the characterization database was small relative to the diversity of the associated wastes. In addition, many of the samples were obtained with the intent of capturing the highest concentration of the constituents of possible environmental concern.]

PHYSICAL CHARACTERISTICS

Key physical parameters for hydrocarbons in environment:

- *Solubility in water*
- *Volatility*
- *Density*
- *Viscosity*
- *Pour point*

WHAT ARE THE PHYSICAL PROPERTIES OF HYDROCARBONS THAT INFLUENCE THEIR MOVEMENT IN THE ENVIRONMENT?

The movement of a hydrocarbon mixture in the environment represents an important aspect of a risk assessment. It is this movement that can result in the exposure of a human or ecological receptor to the chemical. The key physical characteristics of hydrocarbons that effect their movement in the environment include:

- **Solubility in Water:** This property is arguably the most important factor that determines the transport of hydrocarbons in groundwater or surface water.
- **Volatility:** The volatility of a hydrocarbon will dictate its movement with air or other gases.
- **Density:** The density of a hydrocarbon is expressed as its API gravity which is a measure of its specific gravity. The API gravity is inversely proportional to the specific gravity of the compound at 60°F (15°C) and is expressed as an integer, typically ranging from around 9 to 50. It has units of degrees. As a point of reference, fresh water has an API gravity of 10°.

$$\text{API Gravity} = \frac{141.5}{\text{Specific Gravity @ } 60^{\circ}\text{F}} - 131.5$$

- **Viscosity:** This parameter is a measure of the internal resistance of a fluid to flow. Highly viscous material, like molasses, does not flow easily under the forces of gravity while water, a low viscosity material, flows readily. The viscosity of a fluid tends to decrease with an increase in temperature.
- **Pour Point:** The pour point is the temperature below which an oil will not flow in a definite manner. The pour point for most oils arises from the precipitation of wax such that a pasty, plastic mass of interlocking crystals is formed. Wax-free oils have pour points that are dependent upon viscosity only and will tend to thicken to glassy materials as the temperature is reduced and the viscosity increases. Some waxy crude oils may be solid at temperatures as high as 90°F (32°C).

If, and when, a hydrocarbon liquid will move in the environment depends upon the interaction of a number of these parameters. Release of a hydrocarbon liquid, such as crude oil or condensates, to the near-surface unsaturated soil can result in downward gravity-driven migration of the liquid towards the water table. This downward movement will be influenced by the density, viscosity, and pour point of the hydrocarbon. For example, a crude oil with a high pour point might be too viscous to move downward in a cooler climate even though its density would suggest that such movement was possible. If the hydrocarbon liquids are volatile, they may also release individual hydrocarbon compounds into the vapor space that exists within the pores of the soil. If the release of is of sufficient magnitude, hydrocarbon liquid may reach the capillary fringe above the water table, mound and spread horizontally. The extent of spreading is controlled primarily by the hydrocarbon saturation and relative permeability in the subsurface media.

Viscosity and pour point of crude oil suggest that many are not fluid enough to move rapidly, if at all, in the environment.

It is clear from this discussion that the movement of a hydrocarbon liquid through either saturated or unsaturated soil is not a foregone conclusion. While the properties of some hydrocarbons may result in their downward movement towards and dissolution into the water table, the properties of others may prohibit movement of any type. A more detailed discussion of when hydrocarbon liquids become mobile in the unsaturated and saturated soil is presented elsewhere for the interested reader [American Petroleum Institute, 2000a].

WHAT ARE THE NATURE OF THESE PHYSICAL PROPERTIES FOR CRUDE OIL, REFINED PRODUCTS, CONDENSATES, AND E&P WASTES?

Crude Oil

Crude oil is less dense than water with a specific gravity ranging from 0.85 to 0.98 (as compared to 1.0 for water). However, because of the large differences in composition among the various crude oils, the precise density of the crudes can vary substantially. Typical API gravities for crude oil range from 10 to 45.

Crude oil also tends to be a viscous liquid at surface temperatures and pressures. Saybolt viscosities (i.e., time, in seconds, for a 60 milliliter sample to flow through a calibrated orifice at 38°C [100°F]) for four crude oils from California and Prudhoe Bay range from 47 to >6000 seconds. Likewise, the pour points for crude oils are typically high with some that hover around typical seasonal fall and spring temperatures in the United States. The viscosity and pour point are important because they imply that many crude oils are not fluid enough to rapidly percolate through soil.

Crude oil is sparingly soluble in water, with solubility increasing with API gravity. For example, a crude oil with an API gravity of 11° had a total solubility in water of 3.5 mg/L at 25°C (77°F) whereas an oil with an API gravity of 28° had a solubility of 65 mg/L [Western States Petroleum Association, 1993]. However, total solubility is dependent on temperature and the composition of the crude oil.

Refined Products

Many of the refined products of crude oil also have a density of less than 1.0 and API gravities ranging from 15° for No. 6 Fuel Oil to 62° for gasoline. The solubilities of these products in water tend to increase with an increase in API gravity, yielding the following solubility trends for the refined products: gasoline > kerosene > No. 2 diesel fuel > No. 2 fuel oil > No. 6 fuel oil. The viscosity of the refined products also tracks with boiling point and molecular weight, increasing as these parameters increase. The least viscous product is gasoline while the most viscous product is lubricating oil. The pour points of the refined products will depend heavily on the composition of the crude oil (e.g., fraction of wax) although, in general, pour point will increase with viscosity. If anything, an elevated wax concentration in the crude oil would only serve to increase the pour point of the refined products with higher boiling points.

Condensates

Extensive physical property data are not currently available for condensates. However, in broad terms, these hydrocarbon mixtures generally exhibit an API gravity of greater than 45°. This suggests that they are

Solubility ranking of refined products (most to least soluble):

- Gasoline
- Kerosene
- No. 2 diesel fuel
- No. 2 fuel oil
- No. 6 fuel oil

Extensive physical property data for condensates is not available.

not extremely viscous at normal ambient temperatures and that they are relatively volatile and soluble in water. At the same time, composition data from GRI [Hawthorne, et al., 1998] for four condensates revealed that high molecular weight alkanes can be present. The presence of these alkanes would have a tendency to increase both density (i.e., decrease API gravity) and viscosity and decrease both solubility and volatility of the hydrocarbon mixture.

E&P Wastes

The nature of the E&P wastes does not lend itself to an examination of the pure physical properties such as have been described for crude oil, refined products, or condensates. Rather, the majority of the wastes consist of complex soil and liquid matrices that contain hydrocarbons that originated in the crude oil or natural gas. What is of interest, then, is the tendency for these hydrocarbons to be released from these complex matrices and to enter the environment through the groundwater or soil gases. The physical properties of importance are the following characteristics of the individual chemicals: (1) sorption/desorption characteristics, (2) solubility, (3) volatility, and (4) soil saturation. Also of importance is the nature of the waste matrix as specific solids may bind the chemicals more tightly than others. The presentation of these data for all of the hydrocarbons in crude oil or natural gas is beyond the scope of this manual. However, this information can be found elsewhere in the literature [Western States Petroleum Association, 1993].

TOXICOLOGICAL CHARACTERISTICS

All chemicals, including those present in crude oil, refined products, condensates, and E&P wastes, have the inherent potential to impact human health and the environment. However, the presence of a risk depends upon the ability of a human or ecological receptor to come into contact with the chemical and to receive a dose that is sufficiently large to produce an adverse health effect.

WHAT HUMAN HEALTH TOXICITY DATA ARE AVAILABLE?

Limited toxicity data are available from laboratory studies using crude oil and animals. The refined products for which similar data are available are gasoline, jet fuel, and mineral oil [TPHCWG, 1997b]. Essentially no readily available toxicity data of any type exist for either the condensates or the E&P wastes; however, toxicity data are available for several of the individual compounds that are present in these wastes.

Given these available data, toxicity assessments of these materials use toxicity data from a combination of indicator compounds and/or surrogate hydrocarbon fractions. The indicator compounds are

Limited human toxicity data are available for crude oils, refined products, condensates and E&P wastes. This lack of information has required the use of toxicity data for indicator compounds and/or surrogate hydrocarbon fractions.

individual compounds within a mixture that are selected to represent the entire mixture whereas surrogate hydrocarbon fractions are groups of hydrocarbons that are selected for this purpose. These groups of hydrocarbons are often defined in terms of a specific carbon-number ranges. Indicator compounds are most often used to evaluate carcinogenic health effects; surrogate hydrocarbon fractions are used to address non-cancer health effects.

Cancer Health Effects

Potential carcinogens including benzene, selected polycyclic aromatic hydrocarbons (PAHs), and selected heavy metals are the most common indicator compounds that are used to evaluate the carcinogenic health effects associated with crude oil, refined products, condensates, and E&P wastes. Benzene and seven of the sixteen priority pollutant PAHs [i.e., benzo(a)anthracene, chrysene, dibenzo(a,h)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and indeno(1,2,3-cd)pyrene] are used because they are known or suspected carcinogens [ASTM, 1998]. A review of the risk associated with PAHs and heavy metals in crude oil revealed that these chemicals are not likely to pose a carcinogenic health risk at sites that are impacted with crude oil [Magaw et al., 1999a; Magaw, et al., 1999b; Kerr, et. al., 1999a; Kerr, et. al., 1999b]. On the other hand, benzene can be present in crude oil at concentrations that have the potential to impact human health although site-specific considerations have a large impact on whether or not such a risk truly exists at a given site [Rixey, et. al., 1999].

Section 307(A) of the Clean Water Act identifies 126 individual priority toxic compounds that are known as the EPA "Priority Pollutants". Sixteen of these compounds are PAHs, seven of which have been identified as known or suspected carcinogens.

Non-Cancer Health Effects

To evaluate the non-cancer effects of petroleum mixtures, a surrogate approach is used. This approach segregates the petroleum mixture into carbon-number fractions and assigns a toxicity to the fraction based on a single compound or hydrocarbon mixture for which toxicity data exist. The single compound surrogates are selected based upon their presence in the petroleum fraction and the availability of toxicity data. An extensive review of the toxicity data for petroleum hydrocarbons was completed by the TPHCWG and is summarized elsewhere [TPHCWG, 1997b]. This review examined toxicity data for both individual compounds as well as mixtures of petroleum hydrocarbons. On the basis of this review, toxicity characteristics were assigned to a number of different aliphatic and aromatic carbon number fractions. Using these data and a breakdown of the hydrocarbon composition by the carbon-number ranges, the toxicity of any hydrocarbon mixture (e.g., crude oil, refined products, condensates, and E&P wastes) can be estimated [TPHCWG, 1999].

An indepth review of non-cancer human health effects of petroleum hydrocarbons has been conducted and summarized by the TPHCWG [TPHCWG, 1977b].

Development of the ecological risk framework has lagged behind that of human health. A review of the ecological toxicity data for petroleum hydrocarbons was beyond the scope of this document.

WHAT ECOLOGICAL TOXICITY DATA ARE AVAILABLE?

The ecological risk framework is not as well developed as that for human health. For this reason, a review of ecological risk assessment

procedures and ecological toxicity data are considered beyond the scope of this document.

SUMMARY OF KEY DIFFERENCES IN THE CHARACTERISTICS OF CRUDE OIL, REFINED PETROLEUM PRODUCTS, CONDENSATES, AND E&P WASTES

In summary, there are some very important differences in the characteristics of crude oil, refined petroleum products, condensates, and E&P wastes. These differences can have a significant effect on the risk that is associated with their presence at a site.

WHAT IS THE EVIDENCE OF DIFFERENCES IN BULK HYDROCARBON COMPOSITION?

Carbon-Number Range

From a broad perspective, crude oil encompasses a wide spectrum of hydrocarbons compared to its refined products and most of the condensates. As mentioned, a typical carbon-number range for gasoline is only C₅ to C₁₀; diesel, C₁₂ to C₂₈; and condensate, <C₆ to C₃₀. Evidence of these differences can be seen by comparing the gas chromatograms of crude oil (Figure 3), gas condensates (Figure 5), and the refined products of gasoline and diesel fuel (Figure 6). These chromatograms reveal the narrower hydrocarbon distributions that are typical of the refined products and the condensates.

Refined products and condensates have narrower hydrocarbon distributions than crude oils.

Chemical Classes of Hydrocarbons

The gas chromatograms also provide evidence of the differences in hydrocarbon composition that can exist even within a single type of hydrocarbon mixture. The PERF Project 97-08 made a special effort to capture the differences among crude oils by collecting seventy samples of crude oils from all over the world. An indication of how representative these samples were of the general composition of a worldwide set of 636 crude oils is shown in Figure 7 [Tissot B. P. and D. H. Welte, 1978]. The individual data points shown represent the composition of the crude oil samples of the PERF project (51 separate crude oils and crude oil extracts from 6 soil samples). Every one of these data points fall within the 95% frequency distribution envelope that was delineated using the worldwide set of crude oil samples. The composition data points from the PERF project also uniformly cover nearly the entire area within the frequency distribution envelope shown in Figure 7.

The composition of the crude oils in the PERF Project, 97-08, were representative of crude oils from around the world.

FIGURE 6 GAS CHROMATOGRAPHIC FINGERPRINTS OF GASOLINE AND DIESEL FUEL

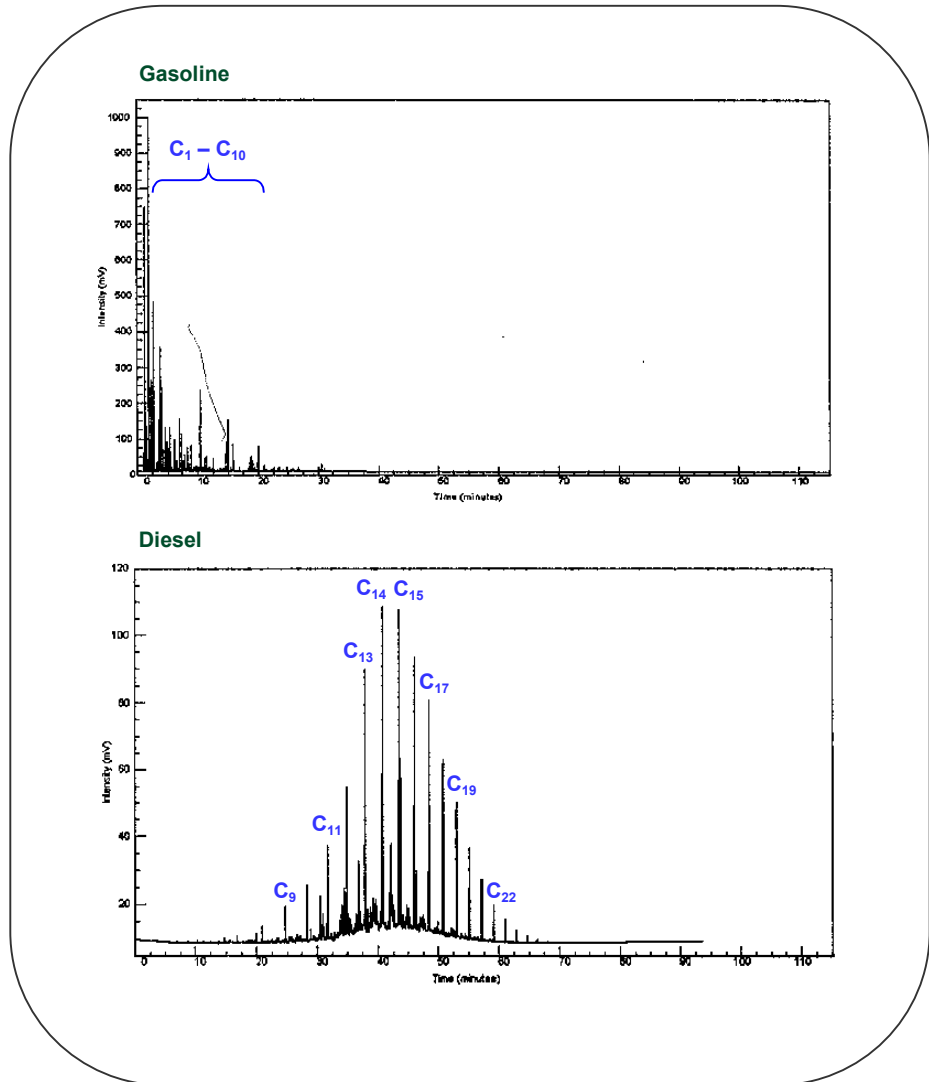
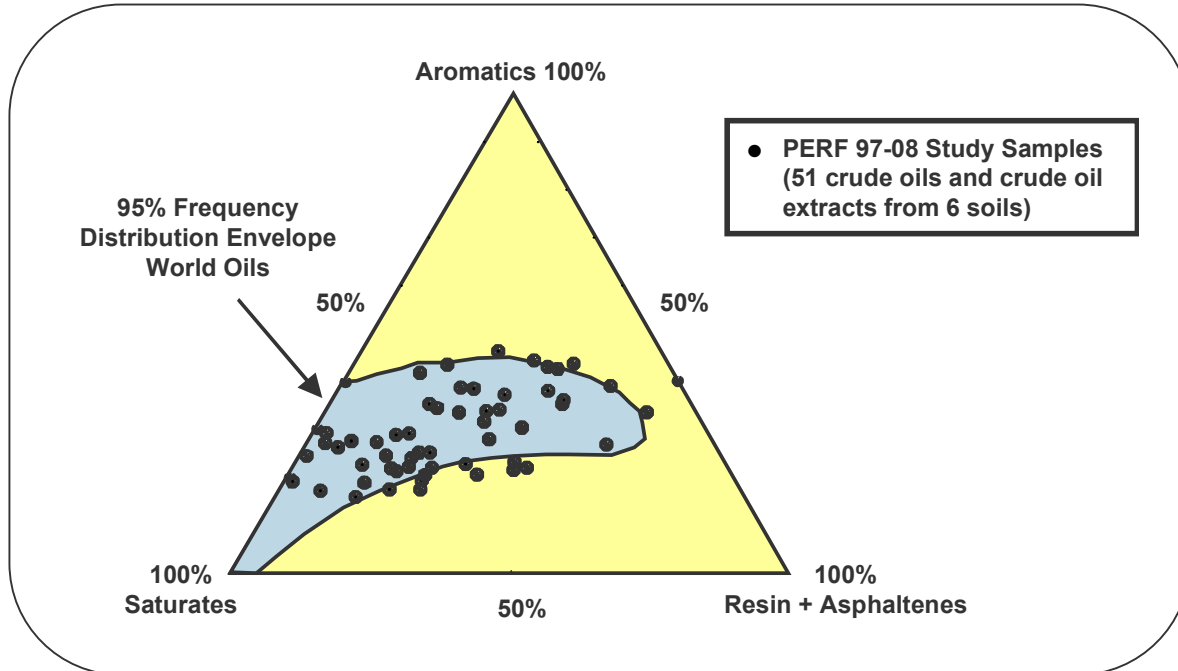


FIGURE 7 COMPARISON OF CRUDE OIL COMPOSITION OF PERF STUDY SAMPLES TO WORLDWIDE (636 CRUDE OILS) SAMPLE SET



API Gravity

Lastly, API gravity, which is quite different between crude oil, refined products, and condensates, is another indicator of the differences in the gross chemical composition of these hydrocarbon liquids. The API gravity for crude oil ranges from <math><10^{\circ}</math> to as high as

API gravity for crude oils ranges from <math><10^{\circ}</math> to as high as

WHAT IS THE EVIDENCE OF DIFFERENCES IN SPECIFIC CHEMICAL COMPOSITION?

On a more chemical-specific basis, concentration differences were also observed for chemicals of concern such as benzene, PAHs (total and carcinogenic), and metals.

Benzene

Condensates and selected refined petroleum products such as gasoline typically have higher benzene concentrations than crude oils. Based on the studies referenced in this document, the range (minimum to maximum) and mean concentration of benzene in these hydrocarbon liquids were as follows:

Mean concentrations of benzene vary from 1,300 mg/kg in crude oil, to 10,000 mg/kg in condensates to 19,000 mg/kg in gasoline.

- Crude oil (68 samples) — Range: Non-detect to 6,000 mg/kg oil (0.6% by weight); Mean of 1,300 mg/kg oil (0.13% by weight).
- Gasoline (124 samples) — Range: 16,000 mg/kg (1.6% by weight) to 23,000 mg/kg (2.3% by weight); Mean: 19,000 mg/kg (1.9% by weight)
- Condensates (14 samples) — Range: 1,500 mg/kg (0.15% by weight) to 36,000 mg/kg (3.6% by weight); Mean: 10,000 mg/kg (1% by weight).

In general, benzene concentrations in the E&P wastes were detected in the low parts per million.

PAHs

PAHs can also be present in hydrocarbon liquids, although typically at low concentrations. The data presented in this document identified a concentration of total PAHs in sixty crude oil samples ranging from traces to 5,000 mg/kg (0.5% by weight). The total PAHs were dominated by the following individual PAHs which were identified in >95% of the samples (mean concentrations in mg/kg oil shown in parentheses — see Table 7 for more detail):

- Naphthalene (422.9)
- Phenanthrene (176.7)
- Fluorene (73.6)
- Chrysene (28.5)
- Pyrene (15.5)
- Benzo(b)fluoranthene (3.9)
- Benzo(k)fluoranthene (0.46)

Range of total PAH concentrations identified in crude oil extended from trace amounts to 5,000 mg/kg oil. Naphthalene was the predominant PAH. Concentrations of carcinogenic PAHs are not significant from a human health point of view.

With regards to seven carcinogenic PAHs, the observed mean concentrations in the crude oil were less than 30 mg/kg, ranging from 0.06 mg/kg of indeno(1,2,3-cd)pyrene to 28.5 mg/kg of chrysene.

The carcinogenic PAH composition of condensates is different from that of crude oil. Only three of the seven carcinogenic PAHs were detected in condensates (benzo[b]fluoranthene, chrysene, and benzo[a]-anthracene), with the highest mean concentration being that of chrysene at 1.8 mg/kg oil. An evaluation of cancer risk due to these seven PAHs at non-residential sites indicate that more than 170,000 ppm (17%) TPH would need to be present in soil for an unacceptable risk to occur.

The concentrations of the 16 priority pollutant PAHs ranged from 200 to 6,000 mg/kg oil, with more than 95 percent of the total being naphthalene. Naphthalene was also detected in the E&P wastes, at much lower concentrations, along with methylnaphthalene, chrysene, and phenanthrene.

Metals

The concentrations of metals in the crude oil samples of PERF were not significant from a risk perspective. Of the 18 heavy metals that were analyzed, all but nickel (20 mg/kg), vanadium (63 mg/kg) and zinc (3 mg/kg) were present at concentrations of less than 1.5 mg/kg.

Metals were also detected at trace levels in 33 samples of eight categories of E&P wastes. Of these detections, only two (arsenic and lead) exceeded risk-based criteria that were previously established by API. No metal concentration data were provided in that report [API, 1996] for any refined products or condensates.

Concentrations of metals in crude oil are not significant from a human health or ecological risk perspective.

Blending Agents and Additives

One unique aspect of the refined products is that some of them also contain traces of blending agents and additives. These materials include chemicals such as alcohols, aminophenols, ethers, and sulfonates.

WHAT IS THE EVIDENCE OF DIFFERENCES IN MOBILITY AND TOXICITY?

The mobility and toxicity of crude oils, refined products, condensates, and E&P wastes are also quite different.

Mobility

The mobility of hydrocarbon liquids in the environment depend upon their density (API gravity), viscosity (resistance to flow) and pour point as well as the properties and characteristics of the geologic strata (e.g., clays, silts, or sands). Hydrocarbon liquids with high API gravities, low viscosity, and low pour points (e.g., gasoline, condensates, and some crude oils) have the potential to be very mobile in a sandy soil but would move very little in a tight clay. Conversely, a liquid with low API gravity, high viscosity, and a high pour point (e.g., mineral oil or some crude oils) would not be very mobile regardless of the nature of the geologic material.

Mobility of hydrocarbons in the environment depends upon the density, viscosity and pour point of the hydrocarbon as well as the characteristics of the geologic strata.

The solubility and volatility of hydrocarbons impact their mobility in groundwater and soil vapor, respectively. These properties track very closely with carbon-number (or molecular weight). Generally, as the carbon-number of the hydrocarbon increases, its solubility in water and volatility decrease. As such, given the wide variability in the carbon numbers of the hydrocarbons among crude oils and between crude oils and refined products and condensates, it is expected that crude oils would demonstrate a wide range of solubilities and volatilities. Evidence of this was provided earlier for crude oil when solubilities in water

Solubility and volatility of hydrocarbons are strongly correlated to carbon-number range (i.e., molecular weight).

ranging from 3.5 to 65 mg/L were documented for two oils with very different API gravities.

Toxicity

There is a similar degree of variability in the toxicity of liquid hydrocarbons due directly to their variable composition and physical characteristics. For example, hydrocarbon mixtures with elevated concentrations of benzene or the aromatic carbon-number fraction from C₈ to C₁₆ have a greater potential to cause human health effects than do hydrocarbon mixtures containing elevated concentrations of the high molecular weight aliphatic carbon-number fraction, C₁₆ to >C₂₅. However, the physical environment can reduce the toxicity of a hydrocarbon by removing the hydrocarbon mixture of concern from the environment through processes such as sorption or biodegradation. It is the action of processes such as these that can eliminate hydrocarbons such as benzene from groundwater before it comes into contact with a human or ecological receptor.

Benzene and the C₈ to C₁₆ aromatic carbon-number fraction have the greatest potential to cause human health effects; the high molecular weight, aliphatic carbon-number fraction of C₁₆ to C₂₅ is not toxic.

PART IV

CALCULATION OF RISK AND RISK-BASED SCREENING LEVELS

WHAT ARE THE KEY COMPONENTS OF THE FOUR ELEMENTS OF THE RISK EVALUATION PROCESS?

The technical elements of the risk evaluation process were described previously and include hazard identification, exposure assessment, toxicity assessment, and risk characterization. Simply stated, a quantitative risk evaluation involves identifying the chemicals of potential concern at a site, simulating their release and movement in the environment, estimating their uptake by humans, and predicting the potential health effects of the exposure.

HAZARD IDENTIFICATION

Hazard identification is accomplished by collecting and reviewing site assessment data and identifying the chemicals of potential concern and the environmental media (e.g., soil, groundwater, air) in which they can be found. It answers the question “What are the potential hazards at the site?”

EXPOSURE ASSESSMENT

The exposure assessment answers the question “Who is exposed to how much of the chemicals of potential concern?” The exposure assessment is a three-step process: (1) the site setting, which depicts the relative locations of the hazards and potential receptors, is characterized, (2) complete exposure pathways are identified, and (3) the magnitude of the potential exposure is estimated.

Characterizing the site setting identifies *who* might be exposed to the chemicals of potential concern. A key question in identifying who these receptors might be is the current and reasonably expected future land use for the site. Historically, regulatory agencies have required site managers to consider all potential future land uses, including residential use, in risk analyses. This is not a reasonable assumption for most E&P sites; more realistic future land uses include ranch land, agricultural land, or park land. More recently, regulatory agencies have focused more clearly on protecting current land uses and have permitted more flexibility in the selection of appropriate future land use scenarios. This has resulted in more flexibility in developing site clean-up criteria.

Chapter Overview:

- Describes four technical elements of the risk evaluation process
- Presents basic equations used to calculate:
 - contaminant intake
 - carcinogenic and non-carcinogenic risk
- Describes risk-based screening levels and presents equations for their derivation
- Describes default assumptions for use in RBSL/risk equations

Exposure pathways are routes by which chemicals at a site can come into contact with potential receptors.

Realistic future land uses for E&P sites include:

- Ranch land
- Agricultural land
- Park land

Exposure assessment is an extremely important element of the risk evaluation because it introduces site-specific factors into the characterization of the site risk.

Once it has been determined who might be exposed to chemicals of potential concern, the next step is to determine **how** they might be exposed. This is a process in which potentially complete exposure pathways are identified. In identifying these complete exposure pathways, the sources of the chemicals at the site are determined and the ways in which they may move around in the environment and be transported to places at which receptors might realistically be exposed are considered. For example, if a crude oil is spilled on soil at a site, a worker in the area may be exposed by direct skin contact with the impacted soil. Alternatively, some of the components of the crude oil may vaporize into air and be inhaled by the worker or they may migrate through the soil into the groundwater and then be transported to a drinking water well at some distance from the site and subsequently ingested. The exposure assessment is important because it introduces site-specific factors into the characterization of the site risk.

The final step of the exposure assessment is to quantify the potential exposure to identified receptors. Standardized intake equations are used in this part of the analysis to answer the final question “To **how much** of the chemicals of potential concern is a receptor likely to be exposed?”

TOXICITY (DOSE-RESPONSE) ASSESSMENT

All chemicals have the inherent ability to cause adverse health effects of some sort, at some dose level; but only some chemicals have the ability to cause cancer.

The toxicity assessment answers the question “What dose levels of the chemicals of potential concern may produce adverse health effects in people or other receptors?” In the toxicity assessment, chemicals are usually evaluated separately for their abilities to cause cancer and other adverse health effects. All chemicals can cause adverse health effects of some sort at some dose level, but only some chemicals have the potential to cause cancer. Most available toxicological data for both carcinogenic and non-carcinogenic chemicals have been generated in the laboratory using pure chemicals that have been added to the food or water of rats or mice. One of the major challenges is in extrapolating these results to situations in which mixtures of chemicals, such as crude oil, may be of concern. A second challenge is in extrapolating the laboratory results obtained in rodents treated with pure chemicals to situations in which people are exposed to chemicals in soil. In both cases, uncertainty factors are included to make certain that chemical toxicity is not underestimated.

Key challenges associated with using toxicity data:

- (1) Extrapolating pure chemical test results to complex mixtures of chemicals*
- (2) Extrapolating pure chemical test results to situations where the chemicals are present in soil*
- (3) Extrapolating test results in animals to humans*

RISK CHARACTERIZATION

The final step of the risk evaluation combines the results of the Exposure Assessment with the Toxicity Assessment to estimate the potential risks posed by the site. The result is a conservative risk estimate that is likely to overestimate the true risks posed by the site. In reality, the true risk is most likely to be much lower than the estimated risk, and may be as low as zero in some cases.

WHAT CALCULATIONS ARE USED TO DETERMINE RISKS TO HUMAN HEALTH?

The calculations used to estimate risk are all based on those originally derived by U.S. EPA. The calculations and the default assumptions that are commonly used in them are specifically designed to provide a result that is protective of human health.

EXPOSURE ASSESSMENT: CALCULATION OF CONTAMINANT INTAKE

The quantitative exposure estimation determines the amount of chemical that is taken in by a receptor for a given exposure route. The potential exposure pathways considered included direct contact with contaminated soils (i.e., inhalation, ingestion, and dermal contact), consumption of groundwater affected by contaminant leaching from site soils, and inhalation of volatiles in outdoor air. In all cases, the calculation of the chemical intake requires knowledge of:

- The concentration of the chemical in the impacted media, i.e., soil (mg/kg), air (micrograms/m³), or water (mg/L)
- The amount of the impacted media that is taken in by the receptor (i.e., liters of air or water or kilograms of soil)

The amount of the impacted medium that is taken in is determined by identifying an exposure event, specifying the quantity of the medium that is taken in per event, and specifying the frequency and duration of the event. The intake is then converted to a dose level by dividing it by the body weight of the receptor and averaging over an appropriate time period. This yields an average daily dose or average lifetime daily dose expressed in mg/kg per day. The averaging time period depends upon the health effect that is being addressed. For example, the averaging time for carcinogenic effects is a lifetime of 70 years. On the other hand, for non-cancer effects, the averaging time is equal to the duration of the exposure (e.g., 25 years for an adult worker).

DERIVATION OF TOXICOLOGICAL DOSE-RESPONSE FACTORS

In estimating risk, the exposure estimate is combined with a toxicological dose-response factor. The dose-response factor depends upon the chemical, the route of exposure, and the health effect that is of concern (i.e., carcinogenic or non-carcinogenic). They are generally derived by U.S. EPA, or other regulatory agencies, and are made available to the public for use by risk assessors. The data on which these factors are based is usually generated in laboratory studies using animals. The dose-response factors derived from these data include reference doses (RfDs) or inhalation reference concentrations (RfCs) for evaluating

Determination of chemical intake for an exposure pathway:

$$I = \frac{C * CR}{BW} * \frac{EF * ED}{AT}$$

where:

- I* = Chemical intake [mg/kg BW-day]
- C* = Chemical concentration [e.g., mg/kg-soil or mg/L-water]
- CR* = Contact rate or the amount of impacted medium contacted per event [e.g., liters/day, mg/day]
- EF* = Exposure frequency [days/year]
- ED* = Exposure duration [years]
- BW* = Body weight of the receptor [kg]
- AT* = Averaging time of the exposure [days]

non-carcinogenic effects and cancer slope factors for evaluating carcinogenic effects as described below:

- **Reference doses (RfDs — mg/kg-day):** Estimate of daily exposure that is likely to be without an appreciable risk of adverse effects during a lifetime of exposure;
- **Reference concentrations (RfCs — mg/m³):** Estimate of a continuous inhalation exposure to the human population that is likely to be without an appreciable adverse effect during a lifetime of exposure; and
- **Oral cancer slope factor [CSF — (mg/m³)⁻¹]:** Slope of the relationship between the oral dose administered in the study and the carcinogenic response.

CALCULATION OF RISK

The risk calculations for non-cancer effects are expressed in terms of a unitless hazard quotient that is calculated using the following equation:

$$\text{Hazard Quotient} = \frac{\text{Average Daily Dose (mg / kg – day)}}{\text{Reference Dose (mg / kg – day)}}$$

Hazard Index, or HI, is the sum of hazard quotients for the individual chemicals of concern at a site. The acceptable limit for HI can also be 1 although Texas recently established 10 as the threshold value [TNRCC, 2000].

The threshold level of acceptability that has been established by the U.S. EPA is the value of 1.0, although some states have established different target values. Hazard quotients greater than 1.0 typically require further analysis or some sort of site action.

The risk calculation for carcinogenic effects is based on a somewhat similar equation:

$$\text{Risk} = \text{Average Lifetime Daily Dose (mg/kg-day)} \times \text{Slope Factor (mg/kg-day)}^{-1}$$

This risk calculation also yields a unitless value. The acceptable individual excess lifetime cancer risk range established by the U.S. EPA is 10^{-4} to 10^{-6} . Many state regulatory agencies have established acceptable risk targets within this range.

WHAT ARE RISK-BASED SCREENING LEVELS (RBSLs) AND HOW ARE THEY DERIVED?

Risk-Based Screening Levels (RBSLs) are chemical-specific concentrations in environmental media that are considered protective of human health. They can be derived from the risk equations by specifying an acceptable target risk level and rearranging the equations to determine the chemical concentration in the environmental medium of concern that achieves this risk level.

The tiered risk-based decision-making approach developed by ASTM relies more on the use of RBSLs for decision making, rather than on an explicit calculation of site risk, as generally used in the classical approach by U.S. EPA. Provided below is an equation, based on those used by ASTM, to calculate an RBSL for non-cancer effects for the exposure pathways of soil ingestion and dermal contact with soil (i.e., RBSL_{ss}):

$$\text{RBSL}_{\text{ss}} \left[\frac{\mu\text{g}}{\text{kg soil}} \right] = \frac{\text{THQ} \times \text{BW} \times \text{AT}_n \times 365 \frac{\text{days}}{\text{year}}}{\text{EF} \times \text{ED} \times \frac{10^6 \frac{\text{kg}}{\text{mg}} \times (\text{IR}_{\text{soil}} \times \text{RAF}_o + \text{SA} \times \text{M} \times \text{RAF}_d)}{\text{RfD}_o}}$$

This equation estimates the maximum concentration of a contaminant in soil that is protective of human health for the exposure pathways that involves both soil ingestion and direct contact with soil. Similar RBSL equations for other exposure pathways (i.e., inhalation of volatiles and particulates, ingestion of groundwater, and inhalation of vapor) are provided in Appendix B.

A couple of items regarding these RBSL equations and their use warrant additional comment. First, the derivation of RBSLs for complex mixtures such as crude oil requires additional manipulations of these equations which will be addressed later in this manual for non-cancer health effects.

Second, there are several factors in the risk equations that address the availability of soil-bound contaminants to the human receptor. These are the dermal relative absorption factor, or RAF_d, the oral relative absorption factor, RAF_o, and the ambient air partition factors for both particulates (VF_p) and vapors (VF_{ss}). These factors are included because the soil tends to bind many of the contaminants and prevent them from coming into contact with the receptor and causing an impact. This matrix effect is caused by the soil, is recognized by the U.S. EPA, and is currently the subject of a great deal of research by universities, industrial consortia, and the U.S. EPA.

The third, and last, point addresses cross media considerations that are relevant to the vapor and groundwater pathways. For both of these exposure pathways, the acceptable contaminant concentrations in the air and groundwater can be used to back-calculate a contaminant concentration in soil that will be protective of these other media. In other words, a contaminant concentration in soil can be determined that will not result in an exceedance of the acceptable contaminant concentrations in air or groundwater. To complete these back-calculations, a volatilization factor (VF, [mg/m³]/ [mg/kg]) and leaching factor (LF,

Definition of parameters for RBSL calculation based on dermal contact with soil:

- THQ = Target hazard quotient for individual constituents [unitless]
- BW = Body weight [kg]
- AT_n = Averaging time for non-carcinogens [years]
- EF = Exposure frequency [days/year]
- ED = Exposure duration [years]
- IR_{soil} = Soil ingestion rate [mg/day]
- RfD_o = Oral chronic reference dose [mg/kg-day]
- RAF_d = Dermal relative absorption factor [unitless]
- RAF_o = Oral relative absorption factor [unitless]
- SA = Skin surface area [cm²/day]
- M = Soil to skin adherence factor [mg/cm²]

Cross media considerations for RBSLs:

- Soil RBSLs to protect groundwater:

$$RBSL_{soil} = \frac{RBSL_{gwater}}{LF}$$

- Soil RBSLs to protect vapor:

$$RBSL_{soil} = \frac{RBSL_{air}}{VF}$$

RBSLs for direct contact with soils in a non-residential setting is often the driver for management decisions at E&P sites.

Selected Risk Assessment Default Values of the U.S. EPA

Parameter	Value
<i>Body Weight</i>	
Adult	70 kg
Child	15 kg
<i>Inhalation Rate</i>	
Adult	20m ³ /d
Child	10 m ³ /d
<i>Water Ingestion Rate</i>	
Adult	2 L/d
Child	1 L/d
<i>Soil Ingestion Rate</i>	
Adult	100 mg/d
Child	200 mg/d
<i>Exposure Frequency</i>	
Residential Setting	350 d/yr
Occupational Setting	250 d/yr
<i>Exposure Duration</i>	
Adult	30 yrs
Child	6 yrs
Occupational	25 yrs

Note:
Child = Ages 1 through 6

[mg/L]/[mg/kg]) are required. The former predicts the amount of contaminant that will partition between the soil and the vapor, while the latter predicts the partitioning from the soil to the aqueous phase [TPHCWG, 1997a].

ARE RBSLS IDENTICAL FOR ALL ROUTES OF EXPOSURE?

The RBSLs will not be the same for all routes of exposure. This is because the dose of a contaminant that a receptor receives depends upon the route of exposure and the concentration of the contaminant in the different environmental media. For this reason, it is possible to have several RBSLs for a contaminant at a given site (i.e., one RBSL for each exposure pathway). The lowest of these RBSLs for the complete exposure pathways at the site is then used for the overall risk-based decisions. Considering the nature and composition of crude oils (i.e., low in volatile or water soluble components that could partition into air or water), it is generally the RBSLs for direct contact with hydrocarbon-impacted surface soils that drive the management of E&P sites. The receptors of concern are most often onsite workers or other non-residential receptors depending upon the current and reasonably anticipated future use of the site.

WHAT ARE THE DEFAULT ASSUMPTIONS THAT ARE USED IN THE RBSL EQUATIONS AND FROM WHERE DID THEY ORIGINATE?

There are a large number of parameters for which values must be available before RBSLs for contaminants in soil can be calculated. Some of these parameters were discussed in the previous paragraph and include:

- The dermal relative absorption factor (RAF_d)
- The oral relative absorption factor (RAF_o)
- The ambient air partition factors for both particulates (VF_p) and vapors (VF_{ss})
- The volatilization factor (Vf, [mg/m³]/[mg/kg])
- The leaching factor (LF, [mg/L]/[mg/kg])

Other required parameters include body weight, exposure frequency, exposure duration, soil and water ingestion rates, air inhalation rates, averaging times for carcinogens and non-carcinogens, skin surface area, and soil-to-skin adherence factor.

The U.S. EPA has developed default values for each of these parameters that can be used if no other site- or chemical-specific data are available. Many state regulatory agencies have also made recommendations for their programs. Where appropriate, default values are available for several potential human receptors including workers, and adult and child residents.

PART V

APPLICATION OF RISK-BASED METHODOLOGIES TO E&P SITES

Chapter Overview:

- Discussion of risk-based analysis of TPH
- Shortcomings of traditional TPH measurements
- Definition of fractions for managing TPH
 - Analysis
 - Mobility/Toxicity
- Application to crude oil, refined products, condensates and E&P wastes

Total Petroleum Hydrocarbon Criteria Working Group led the way in the development of risk-based Assessments of TPH.

Petroleum Environmental Research Forum expanded the efforts of the TPHCWG from refined products to include crude oil.

Traditional approaches for managing E&P sites were based upon protection of plant and water resources.

The Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) convened in 1993 to address the disparity among TPH clean-up requirements being used by states at sites that were impacted with hydrocarbon materials such as gasoline, jet fuels, and lubricating oils. The group, which had over 50 active participants, was led by a steering committee that consisted of representatives from industry, government, and academia. Their goal was to develop scientifically defensible information for establishing TPH clean-up levels in soils that are protective of human health at petroleum-impacted sites. The final approach that evolved from the TPHCWG mirrors the existing tiered risk-based framework of ASTM but expands it by providing a methodology that can address complex mixtures of hydrocarbons rather than just single compounds [TPHCWG, 1999]. Since the TPHCWG methodology has become more well known, it has been applied several times to hydrocarbon-contaminated sites in the railroad industry, the gas transmission industry, and oil and gas E&P facilities [Nakles, et al., 1996; Remediation Technologies, Inc., 1998; McMillen, et al., 1999b].

The Petroleum Environmental Research Forum (PERF), under a project titled *Scientifically Sound Risk-Based Management of E&P Sites* (PERF Project 97-08), made modifications to the TPHCWG methodology [McMillen, et al., 1999a; McMillen, et al., 1999b]. Specifically, PERF enhanced the TPHCWG methodology to address the unique characteristics of crude oils. The ultimate objective of the PERF project was to use the advanced, risk-based scientific methods to establish Tier 1 soil clean-up levels for the wide variety of crude oil types that may be encountered at E&P sites. Once established, compliance with these Tier 1 levels could then be assessed using conventional analyses of TPH.

TPHCWG RISK-BASED METHODOLOGY

WHAT IS THE TRADITIONAL APPROACH FOR MANAGING HYDROCARBON-IMPACTED SOILS AT E&P SITES?

Traditionally, hydrocarbon-impacted soils at E&P sites have been managed based on their total petroleum hydrocarbon (TPH) content. Oil and gas industry guidance on TPH clean-up concentrations at E&P sites was not based upon risk to human health; rather, it was based on the protection of plants and water resources [API, 1993; Currier and

Peoples, 1954; Udo, et al., 1975; Baker, 1970; deOng, et al., 1927; Plice, 1948; Chaineau, et al., 1997; and Saterbak, et al., 1999]. This work illustrated that >10,000 mg/kg TPH from crude oil did not adversely impact the growth of most plants nor pose a risk of leaching to groundwater. Some states adopted a TPH clean-up level of 10,000 mg/kg (1% by weight) based on these results. However, other states used TPH standards as low as 100 mg/kg in soil that are similar to those developed for gasoline leaks at underground storage tank sites for the protection of groundwater. This standard might be applied to an E&P site even though a heavy crude oil, with no potential to leach to groundwater, may have been the only onsite petroleum hydrocarbon. The current research initiatives seek to establish a more consistent technical approach for the management of petroleum hydrocarbons that emphasizes the protection of human health and determines if a TPH concentration of 10,000 mg/kg is indeed protective at E&P sites.

WHAT IS TOTAL PETROLEUM HYDROCARBON OR TPH?

TPH is defined by the analytical method that is used to measure it. Conventional TPH measurement techniques quantify only those hydrocarbons that are extracted by the particular method. To the extent that the hydrocarbon extraction efficiency is not identical for each method, the same sample analyzed by different TPH methods will produce different TPH concentrations.

Conventional bulk measurements of TPH in a sample are sufficient for screening the acceptability of site concentrations, based upon a comparison with existing TPH regulations. However, these bulk measurements are not sufficient to support a human health risk assessment. To illustrate this point, high bulk TPH concentrations can be measured in items that clearly do not pose a risk to human health. For example, TPH concentrations have been measured in many items that can be found throughout nature including grass (14,000 mg/kg of TPH), pine needles (16,000 mg/kg of TPH), and oak leaves (18,000 mg/kg). It has also been measured in household petroleum jelly at concentrations of 749,000 mg/kg. Although these TPH concentrations are substantially greater than many existing TPH standards, none of these materials are considered a risk to human health.

WHAT METHODS ARE USED TO MEASURE BULK TPH IN SOIL AND GROUNDWATER ?

Analytical Methods

Some of the more common methods for the analysis of TPH include: (1) Method 418.1 or Modified 418.1, (2) Method 413.1 for oil and grease, (3) Modified 8015M for Diesel-Range Organics (DRO) and (4) Modified 8015M for Gasoline-Range Organics (GRO) [TPHCWG, 1998a]. Method 418.1 consists of solvent extraction followed by treatment in a silica gel column and infrared spectroscopy; the modified

TPH measurements of several natural materials yield significant TPH concentrations:



Grass — 14,000 mg/kg



**Dried Oak Leaves
18,000 mg/kg**



Pine Needles — 16,000 mg/kg



**Petroleum Jelly
749,000 mg/kg**

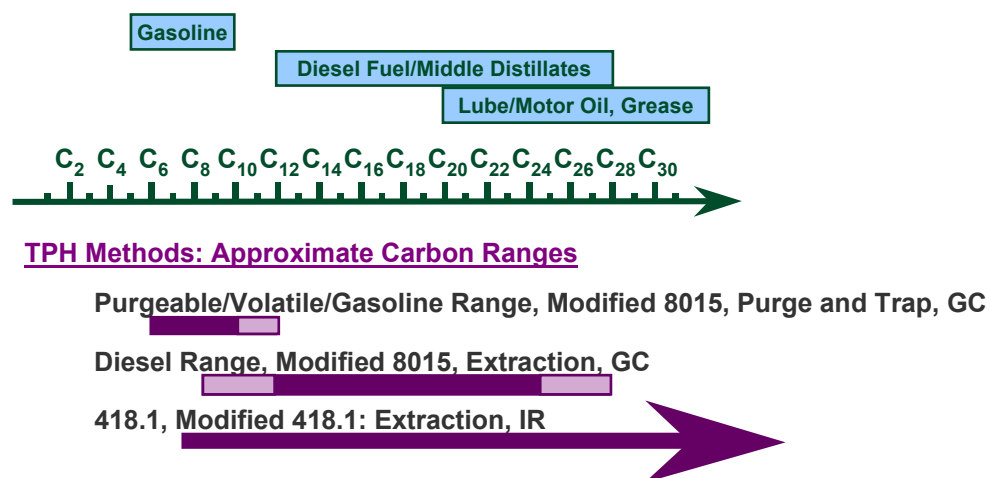
Method 8015 for DRO and GRO are solvent extractions followed by gas chromatography. If it is suspected that the sample is predominately a gasoline (i.e., volatile) fraction, purge and trap sample introduction to the gas chromatograph is often used in the determination of GRO. Method 413.1 is a gravimetric method that consists of solvent extraction, evaporation of the solvent, and a weight measurement.

In addition to these "standard" methods, it should be recognized that there are many permutations of these analyses that have been developed and applied by the individual states. These permutations evolved because, historically, no one universal method for the measurement of petroleum hydrocarbons was available for use. Many of these methods are modified versions of the gas chromatographic methods and are referred to as "modified 8015". In many instances, the regulatory body does not have these methods available in written form.

Shortcomings

Figure 8 shows the overlap between the carbon number ranges of different hydrocarbon products as well as the overlap in the corresponding TPH analytical methods. For example, this figure demonstrates that a TPH method designed for gasoline range organics (i.e., C₆ to C₁₂) may report some of the hydrocarbons present in diesel fuel (i.e., C₁₀ to C₂₈). The same is also true for TPH analytical tests for diesel range organics which will identify some of the hydrocarbons present in gasoline-contaminated soils. Lastly, TPH Method 418.1 covers the complete range from gasoline through lube oil, motor oil, and grease (i.e., C₈ to C₄₀). However, crude oil contains hydrocarbons with carbon numbers that range from C₃ to C₄₅₊ and is not fully addressed even with the use of all three TPH methods.

FIGURE 8. CARBON NUMBER RANGES ADDRESSED BY TPH ANALYTICAL METHODS



WHAT DOES INDUSTRY GUIDANCE TELL US ABOUT TPH CLOSURE CRITERIA?

API has provided guidance for waste management at exploration and production sites [API, 1997]. As part of this guidance, it has delineated acceptable concentrations of hydrocarbons in soil for the waste management practices of landspreading, roadspreading, and burial/landfill. Specifically, the following guidance is provided for TPH and/or oil and grease:

- **Landspreading:** A concentration of 10,000 mg/kg (or 1% by weight) or less of oil and grease is recommended based on the protection of plants, water, and soil microbes. If the TPH or oil and grease have low concentrations of water-soluble organic compounds, TPH concentrations above the 1% limit may also be acceptable.
- **Burial/Landfill:** API recommends that this practice, without the use of a protective liner, be limited to solids or semi-solids that contain low-hydrocarbon content inert materials (e.g., fresh water drilling muds or spent iron sponge). No free oil should be buried or placed in a landfill and the oil and grease content should be limited to no more than 10,000 mg/kg (or 1% by weight).

The guidance for roadspreading does not provide any specific concentration limits for hydrocarbons. Rather, it specifies that the practice should be limited to exempt wastes (see Appendix A) such as tank bottoms or emulsions that have a flash point less than 60°C (140°F), i.e., are not ignitable.

WHAT ARE SOME OF THE TYPICAL TPH CLOSURE CRITERIA THAT HAVE BEEN USED INTERNATIONALLY?

In addition to the state regulations that were presented in Part II, TPH closure criteria have also been established for soils in Canada as well as other international locations. The TPH regulations in Canada range from less than 100 to 5,000 mg/kg [Canadian Council of Ministers, 2000a; Canadian Council of Ministers, 2000b].

Many developing countries such as Venezuela and Indonesia have no regulations for TPH in soil. However, both of these countries do specify the use of the Toxicity Characteristic Leaching Procedure (TCLP) of RCRA for an assessment of the hazardous classification of E&P wastes. Those countries that do have TPH regulations have typically established them by borrowing from the regulations of North America and Europe. In most cases, they have selected the lowest TPH standard, regardless of its applicability, in an effort to ensure that they are being protective. The end result is that some soil standards in these countries are based on oil and grease regulations that were established

Examples of TPH regulations in Canada (mg/kg):

Alberta

1,000 mg/kg — Oil and grease method not specified

British Columbia

(1) *1,000 TEH/100 light HC for Class 1 [TEH = Method 8015 up to C₃₀; Light HC = <C₁₀]*

(2) *2,000 TEH/200 Light HC for Class 2*

(3) *5,000 Oil and grease for Class 3 [special wastes only]*

Class 3 is permitted landfill; Class 2 is commercial or industrial; Class 1 is all others

Examples of soil TPH regulations in other countries:

➤ *Papua New Guinea — 20 mg/kg*

➤ *Nigeria — 50 mg/kg*

➤ *Netherlands (Dutch) — 50 mg/kg (mineral oil and grease)*

in the United States for water, i.e 20 mg/L. Other TPH soil standards, such as the proposed 50 mg/kg limit in Nigeria, were taken from the soil regulations of the Dutch.

WHAT OTHER CRITERIA BESIDES TPH HAVE BEEN USED FOR THE CLOSURE OF E&P SITES?

API also has recommended acceptable criteria for the salt and metals content of exploration and production wastes and/or mixtures of these wastes with soil for the waste management practices of landspreading, road spreading, and burial/landfill [API, 1997]. These criteria are as follows:

- Landspreading: API guidance specifies an electrical conductivity of less than 4 mmhos/cm, an exchangeable sodium percentage of less than 15, and a sodium adsorption ratio of less than 12. pH limits of between six and nine are also specified along with limits for the following metals in mg/kg:
 - Arsenic (41)
 - Barium (180,000)
 - Boron (2 mg/L — Procedures specified by the Louisiana Department of Natural Resources: *Laboratory Procedures for Analysis of Oilfield Waste*, Statewide Order No. 29-B, 1989)
 - Cadmium (26)
 - Chromium (1,500)
 - Copper (750)
 - Lead (300)
 - Mercury (17)
 - Molybdenum (37 — Non-risk interim ceiling established by U.S. EPA on February 25, 1994 [59 *Federal Register* 9050])
 - Nickel (210)
 - Selenium (100 — Site-specific conditions that affect the availability of selenium should be considered if elevated concentrations are present in the waste)
 - Zinc (1,400)
- Roadspreading: No specific concentration limits are established for either salt or metals; however, it is recommended that the metals content should be consistent with that of approved road oils or mixes.
- Burial/Landfill: The recommended criteria for salt in buried or landfilled wastes is an electrical conductivity of less than 4 mmhos/cm. The API guidance also suggests that the metal content of the wastes should be considered although no specific limits are provided for individual metals.

Should the waste or soil/waste mixture be unacceptable for burial or landfill in an unlined unit, another option is to install a liner or to modify the properties of the waste or soil/waste mixture through stabilization or encapsulation.

WHAT IS THE ROLE OF BULK TPH MEASUREMENTS IN E&P SITE MANAGEMENT?

The hazard evaluation that is conducted as part of the risk evaluation of a site requires some level of understanding of the chemical composition of the hydrocarbons that are present in the soil and groundwater. The traditional TPH measurement techniques are not adequate to support this hazard evaluation because they provide no specific information about the hydrocarbons that are detected. In fact, as previously discussed, TPH concentrations can actually represent different fractions of the crude oil, depending upon which methods of TPH analysis are used. In addition, it has been shown that significant TPH concentrations have been measured in many natural materials in the environment that pose no risk to human health (e.g., grass, oak leaves, and pine needles).

However, traditional measurements of bulk TPH can be used to manage a site after Tier 1 RBSLs (Risk-based Screening Levels) have been established using more advanced risk-based methodologies. These Tier 1 RBSLs do not need to be generated on a site-specific basis to reflect the characteristics of the crude oil that is present. PERF Project 97-08 developed a set of risk-based, Tier 1 RBSLs for the TPH of crude oil that could be used to screen the acceptability of all E&P sites. To accomplish this, PERF has conducted extensive hydrocarbon analyses of approximately 70 crude oils from around the world. This information has been combined with exposure assessments that are representative of realistic land uses for E&P sites (i.e., non-residential land uses) to yield conservatively low TPH RBSLs for E&P sites. Since these RBSLs are representative of the TPH and exposure pathways of a wide variety of E&P sites, it is proposed that compliance with these RBSLs can now be assessed using conventional TPH analytical techniques. This approach is completely consistent with that which was recently proposed by the Texas Natural Resource and Conservation Commission [TNRCC] in their draft guidance for the development of protective concentration levels of hydrocarbon mixtures [TNRCC, 2000].

An understanding of chemical composition of hydrocarbons is required for risk-based management of TPH.

Conventional measurements of TPH can be used to manage a site after mixture-specific, Tier 1 RBSLs have been determined using advanced risk-based methodologies.

WHAT IS THE GENERAL RISK ASSESSMENT APPROACH OF THE TPHCWG AND HOW DOES IT ADDRESS THE SHORTCOMINGS OF BULK TPH MEASUREMENTS?

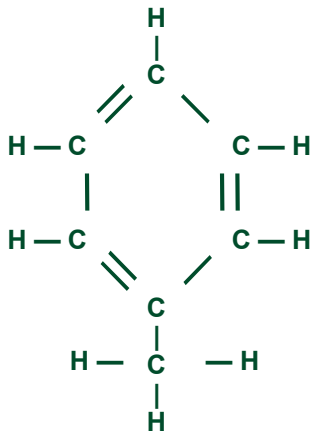
The general approach of the TPHCWG consists of an assessment of risk associated with both cancer and non-cancer health effects.

Cancer Risk

The risk of cancer health effects is examined first by using indicator compounds, such as benzene and the seven carcinogenic polycyclic aromatic hydrocarbons (i.e., benz(a)anthracene, chrysene, dibenz(a,h)-anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and indeno(1,2,3-cd)pyrene), and standard methods of risk assessment. A discussion of cancer health effects as they relate to crude oils will be presented later in this document.

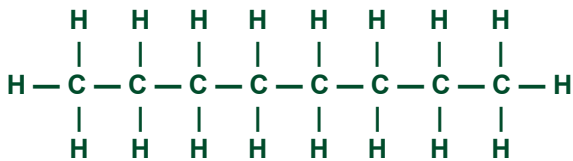
Initial separation of hydrocarbons based on chemical structure:

➤ Aromatic Hydrocarbons



Toluene (C_7H_8 or C_7)

➤ Aliphatic Hydrocarbons



Octane (C_8H_{18})

Non-Cancer Risk

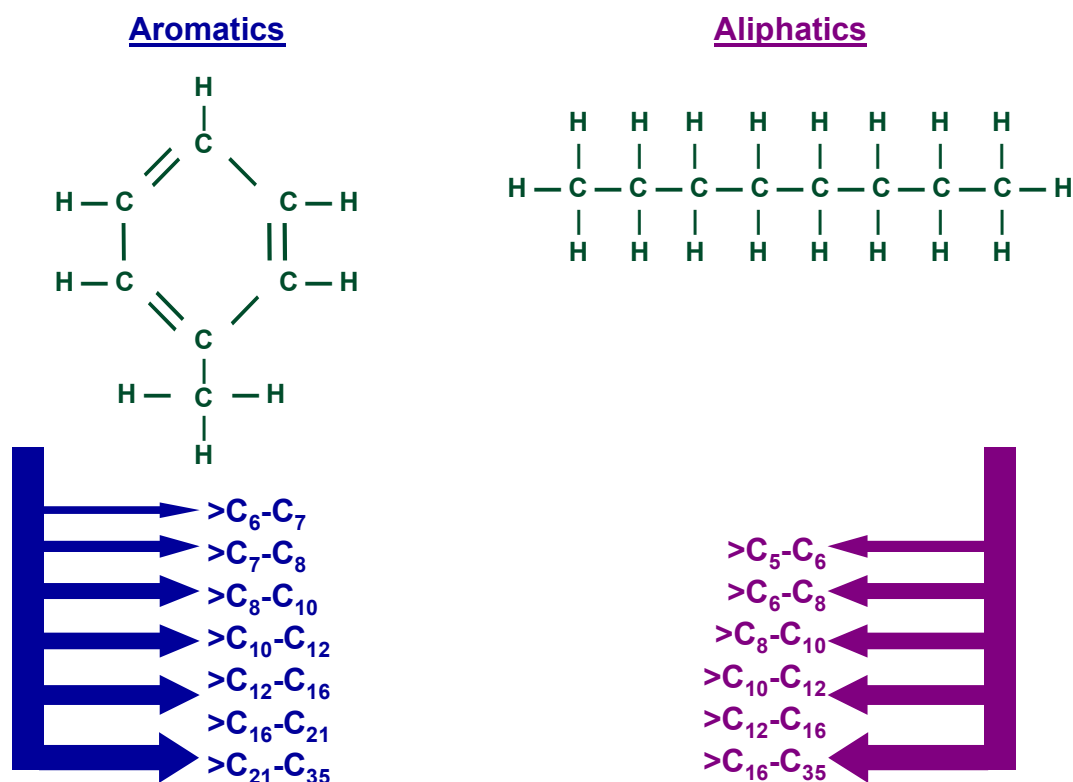
If the risk of cancer health effects is deemed acceptable, the next step in the approach of the TPHCWG is to examine the potential risk of non-cancer health effects. It is in this area that major innovations in the risk assessment methodology have been made. These innovations focused on the development of a better understanding of the composition of the refined products of petroleum, in general, as well as the TPH of these materials. PERF expanded upon these efforts of the TPHCWG by specifically addressing crude oils and condensates.

The complexity of petroleum hydrocarbons represented the major challenge to the TPHCWG. Since it is impossible to analyze complex petroleum hydrocarbon mixtures for all of their constituents and since no one compound could possibly act as a surrogate for these mixtures, the TPHCWG chose to use a fraction approach for assessing their composition. The first step in this fraction approach was to separate the hydrocarbons into two groups based on chemical structure (i.e., aliphatic hydrocarbons and aromatic hydrocarbons). Once segregated into these groups, the aliphatic hydrocarbons were separated into six carbon number fractions and the aromatic hydrocarbons into seven carbon number fractions (Figure 9). Each of the 13 fractions was then treated as if it were a separate compound in the environment.

WHAT BASIS DID THE TPHCWG USE TO DEFINE THE DIFFERENT HYDROCARBON FRACTIONS OF TPH?

The carbon number fractions were identified by selecting groups of hydrocarbons that have similar fate and transport properties, such as solubility and vapor pressure. This was done because of the important role that fate and transport play in determining the exposure of a receptor to a site contaminant. For example, it is the more soluble petroleum compounds that are most likely to migrate to groundwater and represent a risk to humans via the consumption of drinking water. By choosing fate and transport criteria for the definition of the fractions, the TPHCWG ensured that the risk assessment would properly capture the fraction of the hydrocarbon mixture that would be present at the point of exposure for the variety of exposure pathway-receptor combinations that might be present at a site.

FIGURE 9. DETERMINING TPH COMPOSITION: SEPARATION OF CHEMICAL GROUPS INTO CARBON-NUMBER FRACTIONS



Aliphatic and aromatic hydrocarbons were considered separately because their solubility and other fate and transport characteristics are so dramatically different (Table 1). Within each of these groups, the major differences in fate and transport properties were related to the carbon-numbers of the compounds. As shown in Table 1, the properties of the compounds (i.e., solubility, vapor pressure) and their modeled environmental behavior (i.e., coefficient for partitioning to organic carbon (K_{oc}), from soil to water ($PF_{soil/water}$) and from soil to vapor ($PF_{soil/vapor}$)) change by an order-of-magnitude between the different carbon-number fractions. It should be noted that carbon numbers presented in Table 1 represent "equivalent carbon numbers" or ECs. The EC is related to the boiling point of a compound normalized to the boiling point of a normal alkane or its retention on a boiling point gas chromatographic (GC) column. Thus, for compounds where only a boiling point is known, the EC can be readily calculated. For example, the normal alkane, hexane, contains six carbons and has a boiling point of 69°C. Its EC is six. The aromatic hydrocarbon, benzene, also contains six carbons, and has a boiling point of 80°C. Based on its boiling point and its retention in a boiling point GC column, the EC of benzene is 6.5 [TPHCWG, 1997a].

TABLE 1. FATE AND TRANSPORT CHARACTERISTICS OF TPH FRACTIONS (BASED ON EQUIVALENT CARBON NUMBER)

	Solubility (mg/L)	Vapor Pressure (atm)	Log Koc (c/c)	PF* (soil/water)	PF* (soil/vapor)
Aliphatic Fractions					
C ₅₋₆	3.6E+01	3.5E-01	2.9	1E+01	3E-01
> C ₆₋₈	5.4E+00	6.3E-02	3.6	4E+01	9E-01
> C ₈₋₁₀	4.3E-01	6.3E-03	4.5	3E+02	6E+00
>C ₁₀₋₁₂	3.4E-02	6.3E-04	5.4	3E+03	5E+01
> C ₁₂₋₁₆	7.6E-04	4.8E-05	6.7	7E+04	1E+03
> C ₁₆₋₃₅	1.3E-06	7.6E-06	9.0	1E+07	1E+05
Aromatic Fractions					
C ₆₋₇	1.8E+03	1.3E-01	1.9	9E-01	4E+00
> C ₇₋₈	5.2E+02	3.8E-02	2.4	2E+00	9E+00
> C ₈₋₁₀	6.5E+01	6.3E-03	3.2	2E+01	5E+01
>C ₁₀₋₁₂	2.5E+01	6.3E-04	3.4	2E+01	2E+02
> C ₁₂₋₁₆	5.8E+00	4.8E-05	3.7	5E+01	2E+02
> C ₁₆₋₂₁	5.1E-01	7.6E-06	4.2	1E+02	4E+04
> C ₂₁₋₃₅	6.6E-03	4.4E-09	5.1	1E+03	3E+07

Notes:

*Partition factors from soil to water and soil to vapor.

Toxicity literature used was the same literature available to the U.S. EPA during their development of toxicity criteria.

Reference Doses: Estimates of daily exposures (oral or inhalation) to human population that are unlikely to pose significant risk during a lifetime of exposure.

HOW WAS THE TOXICITY OF EACH HYDROCARBON FRACTION ASSIGNED?

Toxicity criteria were developed for each fraction by conducting a thorough literature review of all the data available on pure hydrocarbon compounds, refined petroleum products, and specific hydrocarbon fractions. It is important to note that this toxicity literature is the same literature that was available to the U.S. EPA during their development of toxicity criteria [U.S. EPA, 1997; U.S. EPA, 2000]. The toxicity criteria are expressed as oral reference doses (RfD) in mg/kg/day or as reference concentrations (RfC) in mg/m³ for inhalation exposure. These reference doses and the material that was tested to generate them are summarized in Table 2. In some cases, identical toxicity values were assigned to different fractions. This was due either to the similarity of toxicity findings across fractions or the limitations in the toxicity literature which forced the application of data from one fraction to another. As previously noted, reference doses are estimates of daily exposures to the human population, including sensitive subgroups, that are unlikely to pose a significant risk during a lifetime of exposure.

WHAT ANALYTICAL METHODOLOGY IS USED BY THE TPHCWG TO QUANTIFY THESE HYDROCARBON FRACTIONS?

The TPHCWG developed an analytical technique that is based on SW-846 EPA methods for separating hydrocarbons into fractions using gas chromatography techniques. First, the petroleum hydrocarbon or pentane extract of a soil is separated into aliphatic and aromatic fractions. This chemical separation is accomplished using an alumina column (SW 846 - EPA Method 3611) or a silica gel column (SW 846 — EPA Method 3630). The aliphatic and aromatic fractions are

analyzed separately by gas chromatography and quantified by summing the signals within a series of specific carbon ranges. The gas chromatograph is equipped with a boiling point (i.e., non-polar capillary) column [TPHCWG, 1998a].

TABLE 2. REPRESENTATIVE TOXICITY OF CARBON-NUMBER FRACTIONS

Carbon-Number Fraction		Reference Dose	
Aliphatic	Aromatic	Oral RfD (mg/kg/day)	Inhalation RfC (mg/m ³)
>C ₅ -C ₆ >C ₆ -C ₈		5.0 (commercial hexane, n-hexane)	18.4 (commercial hexane)
>C ₈ -C ₁₀ >C ₁₀ -C ₁₂ >C ₁₂ -C ₁₆		0.1 (JP-8 and other petroleum streams)	1.0 (JP-8 and other petroleum streams)
>C ₁₆ -C ₃₅		2.0 (white mineral oils)	Not applicable due to high molecular weight
	>C ₆ -C ₈	0.2 (toluene)	0.4 (toluene)
	>C ₈ -C ₁₀ >C ₁₀ -C ₁₂ >C ₁₂ -C ₁₆	0.04 (multiple aromatic compounds)	0.2 (aromatic mixture)
	>C ₁₆ -C ₂₁ >C ₂₁ -C ₃₅	0.03 (pyrene)	Not applicable due to high molecular weight

WHY WAS IT NECESSARY TO MODIFY THE TPHCWG ANALYTICAL METHODOLOGY TO DEAL WITH CRUDE OIL AT E&P SITES?

The original version of the TPHCWG analytical methodology did not include hydrocarbons greater than carbon number 35 (C₃₅) (See Figure 9). This is appropriate for most refined petroleum products such as gasoline and diesel. However, the concentration of hydrocarbons with carbon numbers greater than 35 (i.e., C₃₅₊) can be as high as 50% to 60% in some crude oils with low API gravities. Therefore, to conduct a true risk-based analysis of sites where crude oil was present, it was necessary to be able to detect hydrocarbons with carbon numbers greater than C₃₅. This was done by modifying the gas chromatographic technique to quantify hydrocarbons up to C₄₄. Then the fraction >C₄₄ can be determined by distillation or it can be estimated. The hydrocarbon fraction with carbon numbers greater than C₄₄ (i.e., C₄₄₊) is sometimes called the vacuum residuum, since it contains the compounds remaining after the vacuum distillation of crude oil.

HOW WAS THE TPHCWG ANALYTICAL METHODOLOGY MODIFIED TO DEAL WITH CRUDE OILS AT E&P SITES?

The TPHCWG methodology was modified by PERF to deal with the unique characteristics of crude oils. First, the gas chromatography was enhanced to permit the fractionation and detection of hydrocarbons with carbon numbers as high as C₄₄.

Volume percent of vacuum residuum can vary greatly among crude oils:

- ~70%: Crude oil with API gravity of 10°
- <5%: Crude oil with API gravity of 40° to 60°

Next, PERF developed three approaches to determine the mass of hydrocarbon with carbon numbers greater than C_{44} . The most favored approach is to use a distillation analysis of the crude oil. If this information is not available, the next choice is to use a correlation that had been developed for crude oils between the yield of vacuum residuum and API gravity (Figure 10). This correlation was constructed using data from 800 crude oils in the United States [Coleman, et al., 1978]. It can be seen from Figure 10 that the yield (expressed in volume percent) of the vacuum residuum can vary greatly among crude oils. For example, the yield ranges from near 70% for a crude oil with an API gravity of 10° to 5% or less for crude oils with API gravities of 40° to 60°. The last option to determine the C_{44+} fraction is to assign all of the oil, other than the mass of the aliphatic and aromatic carbon number fractions determined by gas chromatography to this heavy fraction.

FIGURE 10. YIELD OF VACUUM RESIDUUM IN 800 CRUDE OILS PRODUCED IN THE UNITED STATES.

Methods for determining mass of C_{44+} hydrocarbons (listed in order of preference):

- Use distillation analysis data
- Use correction between yield of vacuum residuum and API gravity
- Use mass of oil injected into GC less mass of GC-able fraction

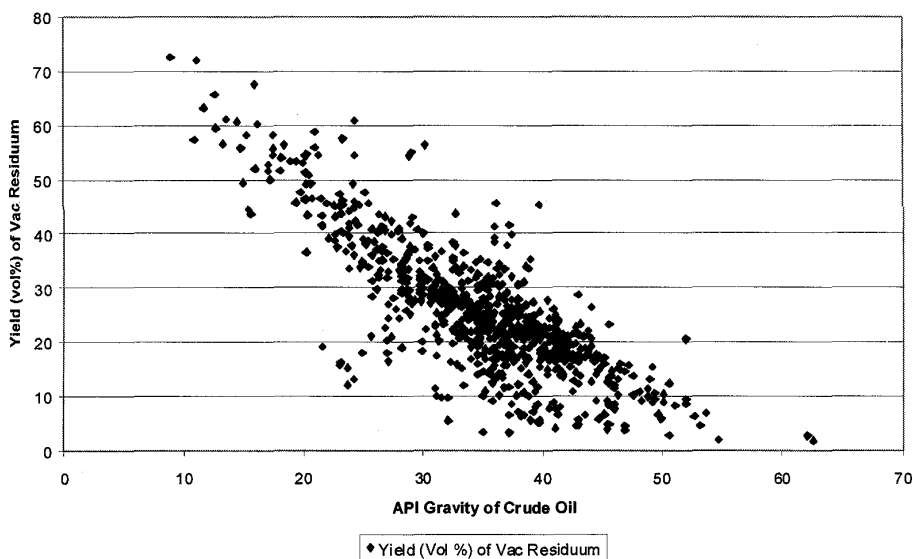
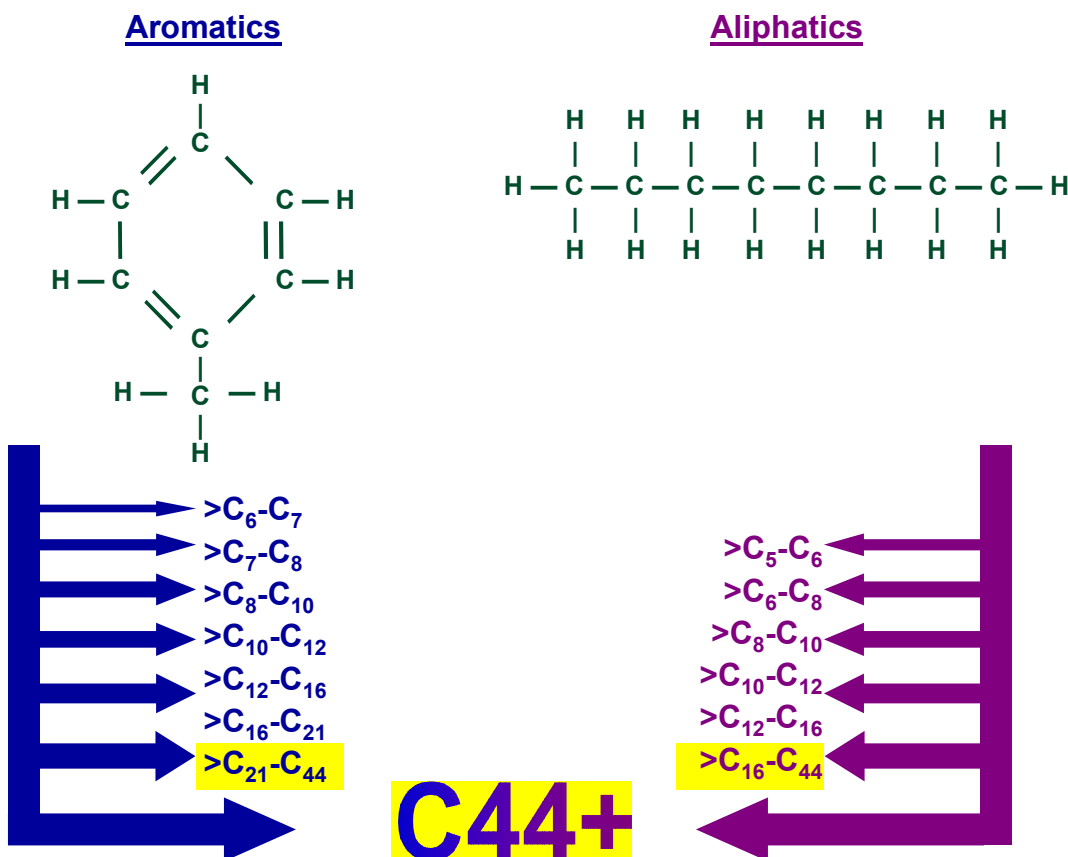


Figure 11 presents the aliphatic and aromatic carbon number fractions that form the basis for conducting a risk-based assessment of the TPH that is associated with crude oils. The major changes that were made to the original carbon number fractions of the TPHCWG shown in Figure 9 are as follows:

- (1) The $>C_{21}$ to C_{35} aromatic carbon number fraction was replaced by a $>C_{21}$ to C_{44} carbon number fraction.
- (2) The $>C_{16}$ to C_{35} aliphatic carbon number fraction was replaced by a $>C_{16}$ to C_{44} carbon number fraction.
- (3) A C_{44+} carbon number fraction was added that included both aliphatic and aromatic hydrocarbons since it was not physically possible to separate hydrocarbons of this size into

separate fractions and the toxicity data were only available for the vacuum residuum fraction as a whole. Most of the resins and asphaltenes reside in the C₄₄₊ carbon number fraction.

FIGURE 11. ALIPHATIC AND AROMATIC CARBON NUMBER FRACTIONS FOR THE ASSESSMENT OF RISK ASSOCIATED WITH CRUDE OIL TPH (highlighted fractions different than fractions of TPHCWG)



WHAT PORTION OF THE TOTAL HYDROCARBON IN CRUDE OIL CAN BE CATEGORIZED USING THE MODIFIED TPHCWG (PERF) ANALYTICAL METHODOLOGY?

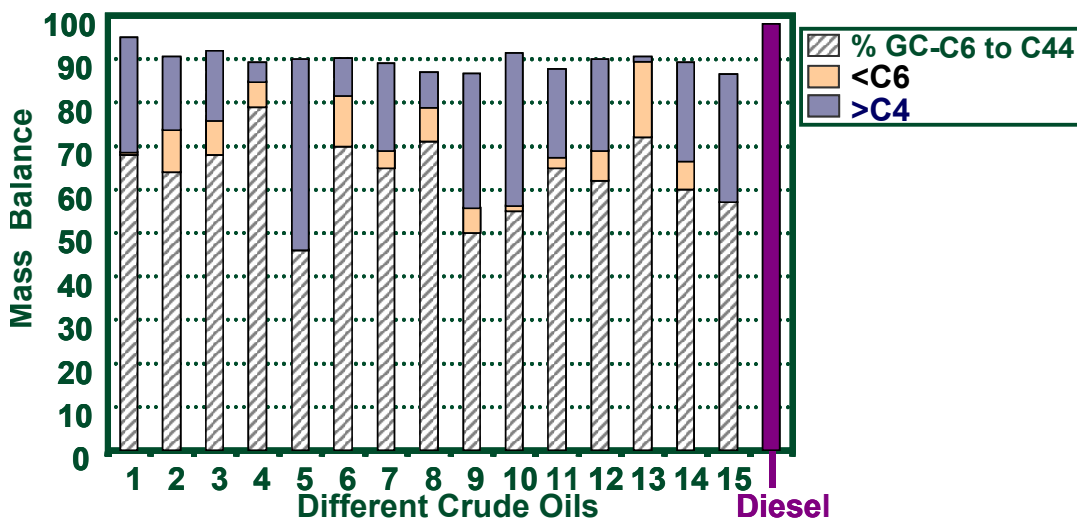
Using the modified analytical method of the TPHCWG, it is now possible to categorize greater than 85% of the hydrocarbon in crude oil compounds into the fractions shown in Figure 11. Figure 12 presents data for fifteen different crude oils to illustrate this point. From this figure, it can be seen that approximately 45 to 80 percent of the hydrocarbons in crude oil can be detected using a gas chromatograph (i.e., carbon numbers from C₆ to C₄₄). The portion of the crude oil that cannot be detected without the application of different techniques is represented by the hydrocarbons with a carbon number less than C₆ or greater than C₄₄. The data in Figure 12 suggest that the former can account for anywhere from 0 to 20% of the crude oil while the latter, from 5% to 45%. Per the previous discussion, the percentage of the

Distribution of hydrocarbons in 15 crude oils:

- 0 to 20%: <C₆
- 45 to 80%: C₆-C₄₄
- 5 to 45%: >C₄₄

C₄₄₊ fraction for each of the 15 crude oils in Figure 12 was determined using distillation. At the same time, greater than 95% of diesel oil can be detected by gas chromatography, alone, further reinforcing the differences in hydrocarbon composition between crude oil and diesel.

Figure 12. Categorization of Crude Oil Hydrocarbon into Carbon Number Fractions



HOW DO THE QUANTITY OF HYDROCARBONS IN EACH FRACTION VARY AMONG DIFFERENT CRUDE OIL PRODUCTS?

Major hydrocarbon fractions in three refined products:

Gasoline

- >C₆-C₁₀ aromatics
- >C₅-C₆ aliphatics

Mineral Oil/Vaseline

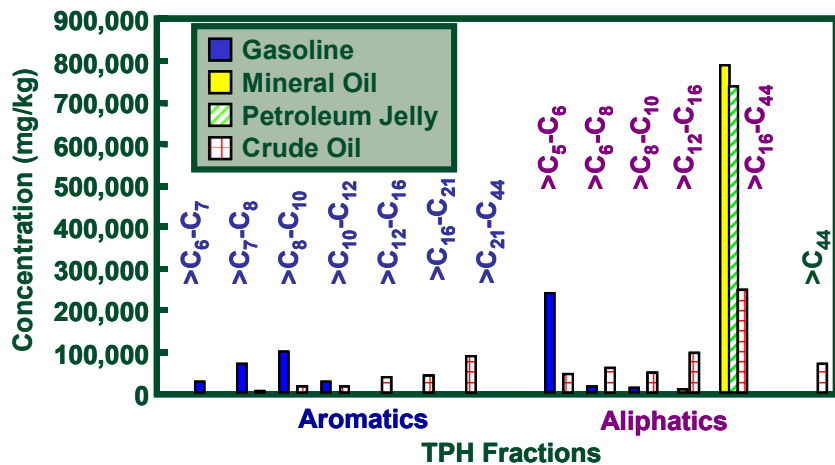
- >C₁₆-C₄₄ aliphatics

Figure 13 provides a comparison of the distribution of the carbon number fractions for the single analyses of four different mixtures of hydrocarbons (i.e., crude oil, gasoline, mineral oil, and petroleum jelly). Not surprisingly, the gasoline is dominated by the lower carbon number fractions of the aliphatic and aromatic hydrocarbons (>C₆ to C₁₀ aromatics and >C₅ to C₆ aliphatics). On the other extreme is the mineral oil and petroleum jelly which consist almost exclusively of the aliphatic fraction, >C₁₆ to C₄₄. Lastly, as expected, the hydrocarbon fractions in a crude oil cover the full range of carbon numbers for both the aliphatic and aromatic fractions as well as a portion of which has a carbon number greater than C₄₄.

HOW WERE THE FATE AND TRANSPORT PROPERTIES AND TOXICOLOGICAL CHARACTERISTICS OF THE C₃₅₋₄₄ AND C₄₄₊ CARBON NUMBER FRACTIONS DETERMINED?

Fate and transport as well as toxicity characteristics for the C₃₅₋₄₄ and C₄₄₊ carbon number fractions were determined in a manner similar to what was done for the original 13 fractions.

FIGURE 13. COMPARISON OF THE DISTRIBUTION OF CARBON NUMBER FRACTIONS IN CRUDE OIL AND SELECTED PRODUCTS



C₃₅₋₄₄ Carbon Number Fraction

There were no transport and toxicity data available for the carbon number fraction, C₃₅₋₄₄. To address this data gap, this hydrocarbon fraction was assigned the characteristics of the next closest aliphatic (>C₁₆ to C₃₅) or aromatic (>C₂₁ to C₃₅) carbon number fractions (See Tables 1 and 2). This is a very conservative assignment since the C₃₅₋₄₄ fraction has a higher molecular weight than either of these two fractions. The actual molecular weight will make the C₃₅₋₄₄ fraction less mobile in the environment than would be predicted by giving it the transport properties of the lower carbon number fractions. Similarly, the C₃₅₋₄₄ fraction will also be less available to cause human health effects following dermal contact or oral ingestion as compared to the lower carbon number fractions.

Transport and toxicity data for C₃₅₋₄₄ fraction:

- Aliphatics: Assigned properties of >C₁₆-C₃₅ aliphatics fraction
- Aromatics: Assigned properties of >C₂₁-C₃₅ aromatic fraction

C₄₄₊ Carbon Number Fraction

As previously mentioned, the C₄₄₊ carbon number fraction is sometimes called the vacuum residuum since it contains the compounds remaining after the vacuum distillation of the crude oil. The vacuum residuum fraction of a crude oil is comprised of very large molecules (those boiling above 600°C [1,112°F]) that are not well characterized as to their compositional make up; however, it is known to contain a mixture of aliphatics, aromatics, metals, and asphaltenes. This fraction is also enriched in heteroatoms (nitrogen, sulfur and oxygen containing compounds) [Altgeit, et al., 1994]. Because of the complex nature, limited mobility, and the small amount of published toxicity data on this fraction, a decision was made to evaluate it as a single fraction, rather than trying to separate it into aliphatic and aromatic groups.

Toxicity and fate and transport values were then selected based on this single fraction.

Toxicity and transport data for C₄₄₊ fraction:

- Toxicity: Identical to pyrene
- Transport:
 - (1) Solubility: 0.0001 mg/L
 - (2) Carbon-water sorption coefficient (K_{oc}): 500,000 cm³/g
 - (3) Henry's Law Constant: 4(10⁻⁸)
 - (4) Leaching factor (soil to water): 1.65(10⁻⁵)[(mg/L)/(mg/kg)]

The primary exposure pathway of concern at most E&P sites involves direct contact and incidental ingestion of impacted surface soils by onsite workers.

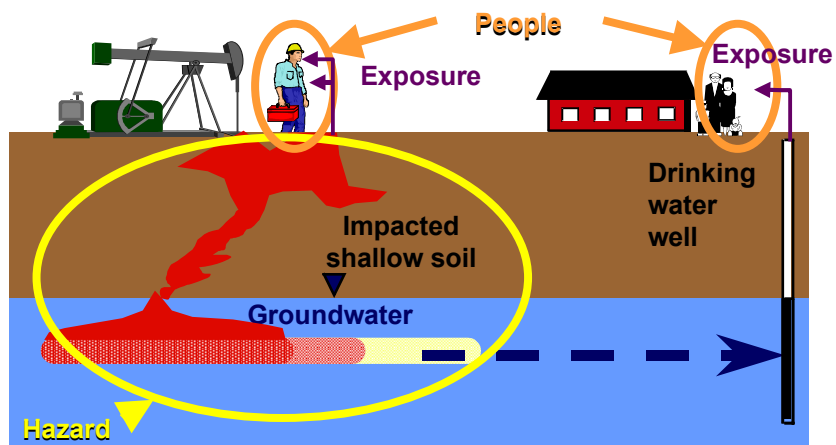
Toxicity. Only two 28-day dermal toxicity studies on vacuum residuum have been published [American Petroleum Institute, 1983]. There are no oral toxicity data available on this heavy fraction of crude oil. Since the U.S. Environmental Protection Agency has not traditionally accepted oral reference doses (RfDs) based on dermal data, the toxicity values for the C₄₄₊ fraction were set at an oral RfD of 0.03 mg/kg/day (the toxicity of pyrene), which is considered a very conservative value. [The conservatism of this assignment is again due to the significant difference in the physical and chemical properties of the pyrene as compared to the heavy molecular weight C₄₄₊ carbon number fraction]. The dermal RfD was set at 0.8 mg/kg/day based on the results of the published dermal toxicity data. No reference concentration for inhalation was defined due to the extremely low volatility of this material.

Fate and Transport. The fate and transport characteristics of the C₄₄₊ fraction were determined as they were for the other carbon number fractions (Table 1). Values were assigned for solubility, carbon-water sorption coefficient, the Henry's Law constant, and a soil to water leaching factor.

WHAT ARE RELEVANT EXPOSURE PATHWAYS FOR AN E&P SITE?

To identify the pathways of most concern to an E&P site, it is useful to develop a conceptual model of the site. This conceptual model identifies the nature and location of the impacted media, the receptors that are present, and the possible pathways for the exposure of these receptors to occur. Figure 14 presents a very simplified illustration of a conceptual model for a generic E&P site. This generic model depicts hydrocarbon-impacted soil and groundwater as the media of concern at

FIGURE 14. CONCEPTUAL MODEL FOR GENERIC E&P SITE



the site. The potential receptors are the onsite worker and nearby residents that are located adjacent to the facility. The potential path-

ways for exposure include the contact of the onsite worker with soil (dermal contact, oral ingestion, and inhalation) and hydrocarbon vapors (inhalation) and the ingestion of drinking water by the local residents. However, due to their remote location, the majority of E&P sites do not have the potential to impact offsite residents and their primary exposure pathways of concern are associated with the onsite worker.

Other exposure pathways and receptors of concern that have also been identified for E&P sites are related to their projected future non-residential uses such as agricultural or park land. These uses introduce other human receptors that are not residents or onsite workers; these receptors may include agricultural workers or park visitors. Similar to the onsite worker at the E&P facility, their exposure to impacted site media would be primarily limited to surface soils.

HOW ARE THE TPH FRACTIONATION DATA USED TO CALCULATE AN RBSL FOR THE WHOLE CRUDE OIL?

The determination of a TPH RBSL for the complex mixture of crude oil requires the composition data for the carbon number fractions and exposure-specific RBSLs for each of these fractions. Using this information, the TPH RBSL for a whole crude oil is determined using an iterative, trial and error procedure. First, an estimate of the **TPH of the crude oil (C_{tot})** is made based on current or previous analytical data or data from other similar crude oils. Then, for any given exposure pathway of concern, the **hazard quotient (HQ_i)** for each carbon number fraction is calculated. This is done by multiplying its **weight fraction in the TPH of the crude oil (f_i)** by the total TPH concentration of the crude oil (C_{tot}) and dividing by the **exposure-specific RBSL for that carbon number fraction ($RBSL_i$)**. The weight fraction of the carbon number fractions in the TPH of the crude oil is determined using the analytical methods that were previously described in this document. The exposure-specific RBSL for the carbon number fraction ($RBSL_i$) is determined from one of the equations presented in Appendix B. The hazard quotients for the individual carbon number fractions are then summed for each pathway of concern to determine the **Hazard Index (HI)**. This sum is compared to a threshold value [Recall that a typical threshold value of 1.0 is often used for this purpose; however, there are situations where individual states have increased this value to 10 (TNRCC, 2000)]. Should the Hazard Index be less than or greater than the threshold of concern, the total TPH concentration of the crude oil (C_{tot}) is revised upward or downward and the calculation is repeated until the threshold value is achieved. The total TPH concentration of the crude oil that yields this value becomes the TPH RBSL for the whole crude oil for that exposure pathway. These calculations are repeated for each pathway of concern to generate pathway-specific TPH RBSLs for the whole crude oil. The lowest (i.e., most conservative) of these pathway-specific RBSLs is then used to evaluate exposure pathways existing at the site.

Iterative Steps in Calculation of TPH RBSL for Crude Oil Using Fraction Data

Step 1: Estimate TPH of crude oil (C_{tot})

Step 2: Calculate *hazard quotient* for individual carbon number fractions for each exposure pathway:

$$(HQ_i) = \frac{f_i (C_{tot})}{RBSL_i}$$

Step 3: For each exposure pathway, sum *hazard quotients* for all carbon number fractions to get the *hazard index* for the pathway

$$HI = \Sigma (HQ_i)$$

Step 4: Compare *HI* to threshold value (usually between 1 and 10)

***HI* $\stackrel{?}{\leq}$ Threshold Value**

Step 5: If *HI* not equal to threshold value, go to Step 1 and adjust estimate of **TPH of crude oil** (up or down). Repeat Steps 2-4 until *HI* is equal to Threshold Value.

Step 6: For each exposure pathway, designate the TPH of crude oil that yields an *HI* equal to the threshold value as the **TPH RBSL**

Step 7: Select lowest **TPH RBSL** from pathways of concern for management of site

There are additional factors that must be considered when conducting the above calculations. For example, the summation of all of the mass fractions of the carbon number fractions must equal unity. Also, the concentration of any carbon number fraction in soil cannot result in hydrocarbon concentrations in pore water and soil vapor above saturation levels. The details regarding phase saturation have been reported elsewhere [TPHCWG, 1999] and are summarized briefly in Appendix C of this document. This detailed information should be consulted before any application of this methodology to a site is attempted.

Lastly, it should be understood that there are some key assumptions regarding the potential interactive toxicological effects of the individual fractions of a hydrocarbon mixture that are implicit in the calculation of the TPH RBSL for the whole crude oil. Specifically, the methodology of the TPHCWG assumes that each carbon-number fraction will affect the same target organ and that the toxic effects are additive. This assumption is considered appropriate for a screening level assessment since different hydrocarbon fractions often affect different target organs, rendering additivity of toxicological effects highly conservative.

WHAT EXPOSURE SCENARIOS AND PATHWAYS ARE IMPORTANT FOR CRUDE OIL AND WHAT ARE THE TPH RBSLS FOR THESE SITUATIONS?

As previously noted, both the current and future land uses will play a role in establishing the exposure scenarios that are important at an E&P site. The TPH RBSLs for crude oil that are determined for the site will be different for these different exposure scenarios because of various assumptions that are made about the receptors and their frequency of contact with the site hydrocarbons. In general, residential exposure scenarios are not considered relevant to most E&P sites and the primary focus of site management is on commercial or other non-residential applications. However, in those instances where residential land use is of concern due to the past history of the site development, the conduct of a site-specific risk assessment to address this scenario may be warranted and should be considered.

Only exposure pathway for TPH that poses a significant risk of non-cancer health effects at E&P sites is direct contact with hydrocarbon-impacted soil.

With regards to non-residential land use, it has been determined that the only exposure pathway for TPH that poses a significant risk of non-cancer human health effects is direct contact with hydrocarbon-impacted soil (i.e., soil ingestion, inhalation of soil particulate, and dermal contact) [McMillen, et al., 199b]. Leaching to groundwater and volatilization to outdoor air can be important pathways for crude oil at non-residential sites but only under certain circumstances [Rixey, et. al., 1999]. This is because most crude oils have low concentrations of the low molecular weight aromatic hydrocarbons as compared to

refined products such as gasoline. It is these fractions that are capable of causing a significant risk (i.e., hazard index above threshold values) for the leaching and volatilization exposure pathways; the other carbon number fractions are either not soluble or volatile enough to result in an exposure of concern.

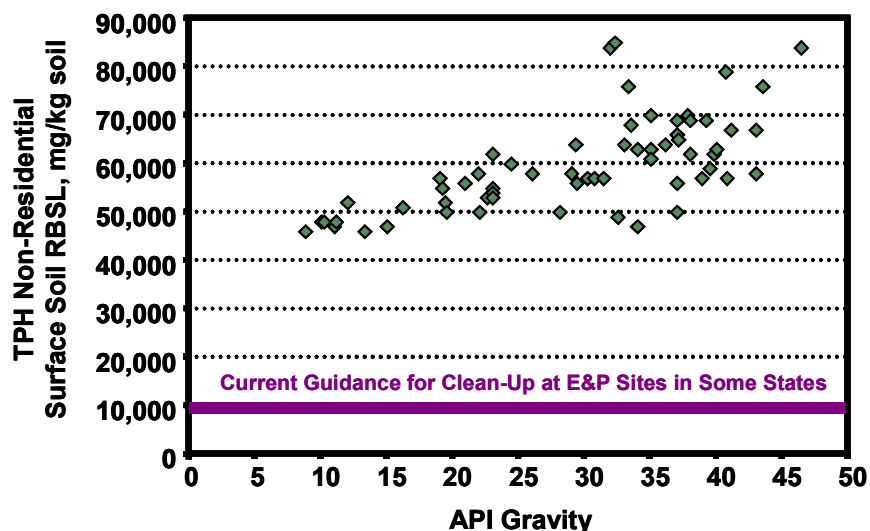
WHAT EXPOSURE PATHWAYS AND TPH FRACTIONS TYPICALLY DICTATE TPH RBSLS FOR CRUDE OIL AT AN E&P SITE?

For nearly all E&P sites, direct contact with surface soil is the primary pathway of concern. This is due to the presence of the high molecular weight, aromatic carbon number fractions in the TPH of the crude oil. From a TPH perspective, the groundwater pathway is not usually a concern since the crude oil is not very soluble in water. In fact, in many instances, the crude oil can be present in soil at residual saturation and not pose a risk via the groundwater pathway.

High molecular weight aromatic and aliphatic carbon number fractions drive TPH RBSLs for direct contact with soil.

An illustration of the effect of TPH composition on nonresidential TPH RBSLs for crude oil in surface soils is presented in Figure 15

FIGURE 15. NON-RESIDENTIAL TPH RBSLS FOR SURFACE SOIL: CRUDE OIL IN SOILS FROM AROUND THE WORLD



Elevated content of high molecular weight aliphatic hydrocarbons present in waxy crude oils yield highest TPH RBSL for soil at E&P model site (i.e., 85,000 mg/kg)

[McMillen, et al., 1999b]. As shown in this figure, all of the TPH RBSLs were equal to or greater than 42,000 mg/kg or 4.2% TPH. The highest TPH RBSLs of 84,000 (8.4%) and 85,000 (8.5%) were obtained for three very waxy crude oils that contained elevated concentrations of high molecular weight aliphatic hydrocarbons. [These hydrocarbons are the least toxic of the carbon number fractions - See Table 2]. The TPH RBSLs in Figure 15 are presented versus their API gravity simply as a way of illustrating the diversity of the crude oils that were examined. As presented, it is evident that there does not appear to be a strong correlation between the TPH RBSL and the API gravity of the crude oil.

HOW DO THE TPH RBSLS FOR CRUDE OIL COMPARE TO TPH RBSLS FOR REFINED PETROLEUM PRODUCTS, CONDENSATES OR ASSOCIATED WASTES?

Refined Petroleum Products

The TPH RBSLs calculated for some products refined from crude oil (gasoline, diesel, mineral oil, baby oil, and petroleum jelly) under a non-residential exposure scenario are shown in Table 3. In this example, the limiting exposure pathway (i.e., the exposure pathway with the lowest TPH RBSL) for gasoline is leaching to groundwater, and the non-residential TPH RBSL for this pathway is 1,800 mg/kg soil. For all the other products, the limiting exposure pathway is direct contact with surface soil. The non-residential TPH RBSLs for this pathway range from 53,000 (or 5.3%) for diesel oil to 1,000,000 mg/kg (or 100%) for petroleum jelly. The elevated TPH RBSLs for both mineral oil and petroleum jelly confirm the appropriateness of the assumptions used for the exposure pathways and for the toxicity and transport/fate parameters of the TPH fractions, since both of these materials are known to be safe for human contact and/or ingestion. petroleum jelly and mineral oil contain only high molecular weight aliphatic compounds and no aromatic hydrocarbons (the more toxic and water soluble hydrocarbons), thus it is reasonable for them to have high TPH RBSLs.

Benzene concentrations were determined for over 124 samples of gasoline:

- Concentration range was 1.6 to 2.3%
- Average concentration was 1.9%

TABLE 3. TPH RBSLS FOR SELECTED REFINED PRODUCTS OF CRUDE OIL (MG/KG)

	Non-Residential Scenario		
	Leaching to GW	Vaporization to Outdoor Air	Surface Soils
Gasoline*	1,800	NL	NL
Diesel*	NL	NL	53,000
Baby Oil	NL	NL	610,000
Mineral Oil	NL	NL	890,000
Petroleum Jelly	NL	NL	1,000,000

Notes:

NL: Not limiting exposure pathway.

*These RBSLs were derived based upon single samples of these hydrocarbon mixtures. The RBSLs will likely vary (either up or down) for other gasolines or diesels depending upon their composition.

In contrast, gasoline, consists primarily of hydrocarbons ranging from C₅ to C₁₀ and contains aromatic hydrocarbons including benzene (2.7 weight percent for this particular sample). As such, it has the lowest TPH RBSL. [The average benzene content of 124 gasoline samples was determined to be 1.9% with a minimum of 1.6% and a maximum of 2.3% (TPHCWG, 1998b)]. Diesel, which contains approximately 30 percent aromatics and very low levels of benzene, has an intermediate TPH RBSL of 53,000 mg/kg, again limited by direct soil contact and not by the groundwater leaching pathway.

Gas Condensates

TPH RBSLs were also calculated under a non-residential exposure scenario for fourteen gas condensates taken from across the continental United States. These TPH RBSLs are summarized in Table 4. It can be seen from these data that the limiting exposure pathway for the gas condensates is direct contact with surface soil, which was also the limiting pathway for all of the crude oils and all of the refined crude oil products except gasoline. The values for the TPH RBSLs of the gas condensates ranged from 53,000 to 190,000 mg/kg with the majority of them (i.e., 12 of 14) falling between 50,000 and 72,000 mg/kg. These values are consistent with those calculated for diesel oil (Table 3) and all of the crude oils that were examined (Figure 15).

Non-residential TPH RBSLs for gas condensates are very similar to those for all of the crude oils and for diesel oil (i.e., 50,000 to 100,000 mg/kg).

TABLE 4. TPH RBSLs FOR SELECTED GAS CONDENSATES (MG/KG)

Condensate	Non-Residential Scenario		
	Leaching to Groundwater	Vaporization to Outdoor Air	Surface Soils
1	NL	NL	61,000
2	NL	NL	63,000
3	NL	NL	63,000
4	NL	NL	69,000
5	NL	NL	71,000
6	NL	NL	58,000
7	NL	NL	68,000
8	NL	NL	64,000
9	NL	NL	53,000
10	NL	NL	55,000
11	NL	NL	96,000
12	NL	NL	100,000
13	NL	NL	190,000
14	NL	NL	65,000

Notes:

NL: Not limiting pathway

Associated Wastes

Wastes from two different production sites plus soil samples from three sites were evaluated using the TPH risk assessment methodology. The non-residential TPH RBSLs that were generated are presented in Table 5 along with those of the crude oils that were produced at the five sites. Before reviewing the information that is presented in Table 4, it is important to note that the limiting exposure pathway was direct contact with surface soils for all of the materials that were examined.

The data show that the TPH RBSLs for the E&P wastes (tank bottoms, oiled road material, oily soils, cyclone separator sludge, and slop oil) have similar to or higher TPH RBSLs than their parent crude oils. This suggests that the TPH RBSLs for crude oil should provide a conservative criterion for managing wastes that are present in soils at E&P sites.

Texas Natural Resource and Conservation Commission recently issued draft guidance stating that conventional TPH measurements can be used to evaluate a site providing TPH RBSLs have been determined for the hydrocarbon mixture at the site using the fractionation approach.

WHEN IS IT NECESSARY TO USE THE RISK-BASED ASSESSMENT OF TPH RATHER THAN CONVENTIONAL TPH MEASUREMENTS OR ASSESSMENTS?

The use of conventional measures of bulk TPH is more than adequate for site management purposes providing that RBSLs have been determined for the specific hydrocarbon mixture at the site or for specific types of hydrocarbon mixtures, e.g., transformer mineral oil [TNRCC, 2000]. If it is suspected that multiple sources of different hydrocarbons may have been present at the site (e.g., chromatographic fingerprints of the bulk TPH changes across the site), then it may be necessary to calculate more than one RBSL for each exposure pathway of a site. However, in general, only one sample from each potential source area needs to be evaluated using the more advanced, risk-based assessment of TPH composition.

TABLE 5. NON-RESIDENTIAL TPH RBSLS FOR CRUDE OIL AND THEIR ASSOCIATED WASTES (MG/KG)

	Leaching to Groundwater	Vaporization to Outdoor Air	Surface Soils
Field #1			
Crude Oil	NL	NL	82,000
Tank Bottoms	NL	NL	84,000
Oily Soil	NL	NL	76,000
Oiled Road Material	NL	NL	96,000
Field #2			
Crude Oil	NL	NL	52,000
Cyclone Separator Sludge	NL	NL	59,000
Slop Oil	NL	NL	61,000
Field #3			
Crude Oil	NL	NL	63,000
Oily Soil	NL	NL	100,000
Field #4			
Crude Oil	NL	NL	64,000
Oily Soil	NL	NL	77,000
Field #5			
Crude Oil	NL	NL	61,000
Oily Soil	NL	NL	75,000

NL: Not limiting pathway.

In lieu of generating a mixture-specific RBSL for a site, the site manager can elect to use a pre-determined RBSL provided that it was generated using a petroleum mixture that is similar to the one of interest at his site. For example, the State of Texas has developed an RBSL specifically for transformer mineral oil [TNRCC, 2000]. This Tier 1 RBSL was based on actual data that were collected on hydrocarbon-impacted soils by the utility industry. Any owner of a site that has transformer mineral oil as a source of hydrocarbon impacts can now use this RBSL to conduct a Tier 1 screening of his site.

The TNRCC has invited other industries to generate similar data for gasoline, diesel, and other petroleum hydrocarbons. The objective of

these efforts is to develop Tier 1 RBSLs for these materials that could be used by a site manager to rapidly evaluate site conditions. This would be done by comparing conventional measurements of TPH with the RBSLs in the table. Due to the importance of weathering on the environmental behavior, and hence risk, of petroleum hydrocarbons, the TNRCC has stated a preference for Tier 1 RBSLs to be based on representative compositions of weathered hydrocarbons that are present in the soil. (More about the importance of weathering on the determination of TPH RBSLs is presented as part of the benzene discussion in the next section.) Clearly, the data that have been generated as part of PERF 97-08 could be used to calculate Tier 1 RBSLs for crude oil. This information could then be used to conduct Tier 1 risk assessments at E&P sites using conventional measurements of TPH.

PERF 97-08 data base for crude oil provides a basis to establish a table of Tier 1 RBSLs for the management of E&P sites.

HOW IMPORTANT ARE THE RISKS ASSOCIATED WITH METALS, POLYCYCLIC AROMATIC HYDROCARBONS, AND BENZENE IN THE CRUDE OIL ?

The risk-based methodology for TPH that is presented in this document addresses the non-cancer health effects for humans. The cancer risk associated with certain PAHs, benzene and metals are addressed separately. The document does not address ecological risks of any type. Ecological risks associated with E&P sites are currently being addressed by API, GRI, and PERF through new research initiatives. As such, this area of risk is not addressed in this document.

Ecological risks are currently the topic of a new research initiative of PERF, GRI, and API.

Metals

A recent risk evaluation of the presence of metals in crude oils indicated that they are unlikely to be a major risk management considera-

Assessment of 26 crude oils indicate that metal concentrations in crude oil will not drive the risk at E&P sites at TPH concentrations of 10,000 mg/kg.

TABLE 6. SUMMARY OF METALS CONCENTRATIONS (MG/KG OIL) IN 26 CRUDE OILS

	Ag	As	Ba	Be	Cd	Co	Cr	Cu	Hg
Mean	0.15	0.06	0.052	ND	0.010	0.27	0.270	0.081	0.06
Minimum	0.05	ND	ND	ND	0.003	ND	ND	0.012	ND
Maximum	0.30	0.57	0.368	ND	0.026	1.3	1.43	0.241	1.56
Detection Freq. (# per 26 Oils)	26	7	19	0	26	16	25	26	1
Method Detection Level	0.010	0.080	0.001	0.005	0.002	0.010	0.005	0.010	0.010

	Mo	Ni	Pb	Sb	Se	Sn	Tl	V	Zn
Mean	0.77	19.69	0.032	0.011	0.16	1.37	0.000	62.75	2.92
Minimum	0.30	0.05	0.005	ND	ND	0.04	ND	0.13	ND
Maximum	4.0	93.0	0.149	0.055	0.52	9.66	0.004	370.0	10.9
Detection Freq. (# per 26 Oils)	26	26	26	21	24	26	3	26	23
Method Detection Level	0.020	0.020	0.001	0.001	0.02	0.010	0.002	0.020	0.080

ND = Not Detected

tion at crude oil spill sites [Magaw. et al., 1999a; Magaw, et, al., 1999b]. The evaluation involved a total of 26 crude oils that were analyzed and found to contain very low levels of metals (Table 6). Evaluation of the human health risk associated with soil containing these crude oils showed that the potential risk due to the presence of the metals was not significant at total crude oil concentrations in soil above 10,000 mg/kg, measured as total petroleum hydrocarbons (TPH). The amount of metals in 10,000 mg/kg TPH would also be protective of soil invertebrates, plants, and soil microbial communities as defined by published ecological soil screening levels.

Polycyclic Aromatic Hydrocarbons

Similar to the analysis of metals in crude oil, an analysis of 70 crude oils revealed the presence of very low concentrations of priority pollutant PAHs including the seven carcinogenic PAHs (Table 7) [Kerr, et al., 1999a; Kerr. et al., 1999b]. A screening of the human health risk associated with the presence of the carcinogenic PAHs in crude oil-contaminated soil showed the risk was not significant at TPH concentrations up to 170,000 mg/kg at non-residential sites. Even when the more restrictive exposure and toxicity parameters of the State of California were used, the acceptable levels for crude oil in soil based on the potential human health effects of PAHs were determined to be well above 10,000 mg/kg. This indicates that the low levels of PAHs in crude oils are not likely to be a major risk management consideration at crude oil spill sites and that TPH RBSLs of 10,000 mg/kg will be protective of human health with a considerable safety factor. In cases where groundwater protection may be of concern, the potential for naphthalene to leach to groundwater may need to be evaluated separately. Overall, these results suggest that there is no compelling evidence to conduct routine PAH analyses at E&P sites.

Low concentrations of PAHs in crude oil are unlikely to be a major risk at E&P sites. These results suggest that there is no compelling evidence to routinely conduct PAH analyses at these sites.

Benzene

An understanding of the impact of benzene in terms of cancer risk on the management of residual hydrocarbons at E&P sites is continuing to evolve. Current work to examine this issue is building upon previous efforts that were focused on the management of underground storage tanks (UST). Since the UST programs usually dealt with refined petroleum products such as gasoline, the majority of the recent work has been to delineate the key differences that exist when crude oil is the petroleum hydrocarbon of concern.

Average benzene concentration in 69 crude oil samples was 1,340 mg/kg oil; in condensates, 10,300 mg/kg.

Presence of Benzene at E&P Sites. Benzene concentrations were measured in a total of 69 crude oils and 14 natural gas condensates [Rixey, 1999]. Its concentration in the crude oil ranged from non-detect (<1.4 mg/kg oil) to 5,900 mg/kg oil, with a mean concentration of 1,340 mg/kg oil. In contrast, the maximum concentration in the natural gas condensates was 35,600 mg/kg of condensate (3.56%) with a mean concentration of 10,300 mg/kg.

TABLE 7. PAH CONCENTRATIONS (MG/KG OIL) IN 60 CRUDE OILS

PAH	Minimum	Maximum	Mean	Detection Frequency
Naphthalene	1.2	3700	422.9	60
Acenaphthene	ND	58	13.9	48
Anthracene	ND	17	3.4	24
Phenanthrene	ND	916	176.7	59
Fluorene	1.4	380	73.6	60
Benz[a]anthracene	ND	38	5.5	40
Fluoranthene	ND	26	3.9	24
Chrysene	4	120	28.5	60
Pyrene	ND	82	15.5	58
Dibenz[a,h]anthracene	ND	9.2	1.0	28
Benzo[a]pyrene	ND	7.7	2.0	45
Benzo[b]fluoranthene	ND	14	3.9	60
Benzo[k]fluoranthene	ND	7	0.46	56
Indeno[1,2,3-cd]pyrene	ND	1.7	0.06	4
Benzo[ghi]pyrene	ND	9.6	1.53	38

PAHs in **bold** font have been shown to be carcinogenic in laboratory animals [ASTM, 1998].

ND = Below detection limits.

Tier 1 RBSLs. Using the risk evaluation methods presented in this document, it has been determined that TPH RBSLs for complex hydrocarbon mixtures (e.g., crude oil or gas condensates) will be based on direct contact with soil as the limiting exposure pathway as long as the benzene concentration in the parent mixture is less than 300 mg/kg of hydrocarbon mixture (i.e., oil or gas condensate). Above this threshold limit, the leaching of the benzene to groundwater becomes the limiting exposure pathway. As such, if it is known that the parent hydrocarbon mixture had benzene concentrations of 300 mg/kg or less, then it would not be necessary to measure benzene at the site. In these instances, the TPH RBSL would be dictated by the composition of the carbon-number fractions of the TPH as described in this document. To put this in perspective, approximately one-third of the 69 crude oils (i.e., 25 of 69 oils) examined in this report contained less than 300 mg/kg of benzene and of those crude oils with an API gravity of less than 20°, only one contained >300 mg/kg of benzene. In contrast, all of the gas condensates had benzene concentrations exceeding 300 mg/kg.

TPH, alone, will drive risk at E&P sites when benzene concentration is <300 mg/kg in crude oils and condensates. One-third of the 69 crude oils had benzene concentrations below that threshold.

At benzene concentrations above 300 mg/kg in crude oil or natural gas condensates, the simple Tier 1 analysis indicates that benzene is the limiting compound in controlling risk, where the limiting exposure pathway is often the leaching of benzene from soil to groundwater. In general, the equivalent TPH RBSLs derived from a Tier 1 analysis

decrease to below 10,000 mg/kg of soil when these concentrations of benzene are present.

Other Considerations: Weathering and Natural Attenuation. Benzene concentrations in hydrocarbon-impacted soil at E&P sites can be significantly less than the concentrations in the fresh crude oil. This is due largely to the weathering that occurs following the initial contact of the crude oil with the soil. This weathering process can have a significant impact on the determination of the RBSLs. As a point of reference, the difference in the benzene concentration between the fresh crude oil and the TPH in the soil for these two examples was 2,800 mg/kg of oil versus 1.2 mg/kg of TPH and 1,200 mg/kg of oil versus 310 mg/kg of TPH, respectively [Rixey, et al., 1999].

Weathering and natural attenuation processes can further reduce the risk associated with benzene at an E&P site, thereby resulting in an increase in TPH RBSLs in those instances where benzene is present in concentrations >300 mg/kg.

Natural attenuation is the dilution and degradation of the benzene in water or vapor migrating from a source area (such as the zone of an oil spill or release in soil) through the adjacent soil and groundwater. Natural attenuation includes biodegradation. Benzene is naturally consumed in this process by soil microbes and disappears from the environment. Natural attenuation of BTEX has been extensively studied in groundwater and summarized [API, 1998]. Most benzene groundwater plumes in consolidated sediments are attenuated to levels below concern within several hundred feet of a source zone due to natural attenuation.

In addition to natural attenuation in groundwater, benzene can also significantly degrade and attenuate as it is transported through the vadose zone [API, 1996]. This further increases the conservatism presumed in the above simple Tier 1 analysis. While the understanding of natural attenuation processes in unsaturated soils is still progressing, recent estimates of benzene natural attenuation for gasoline releases in soil [API, 2000b] suggest the process is very significant. Impact to groundwater from a release would be negligible unless the gasoline itself migrated to the water table or if limited biodegradation occurred (due to a lack of oxygen) in the vadose zone.

RBCA TOOLS FOR THE E&P INDUSTRY

There are a number of commercially available software tools for estimating risk-based screening levels for complex mixtures of hydrocarbons and single indicator chemicals, such as benzene, when they represent the primary risk issue at a site. Typically these models are used for Tier 2 and 3 analysis. Two such models are the API DSS [API, 1999] or BP Risk [Spence, L. R. and T. Walden, 1997].

It is imperative that the user fully understands the underlying methodology and assumptions of the software tools. Some key questions that should be asked are:

- Is the output in the form of a single TPH RBSL for the whole crude oil? (Some software tools may only provide a TPH RBSL for each carbon-number fraction.)
- Are the carbon-number fractions specified consistent with those accepted by the state regulatory agency and supported by acceptable analytical protocols?
- How is the heavy fraction (i.e., hydrocarbons with a carbon-number great than C₄₄) handled?

The important point is to recognize that the existing tools do a number of calculations and numerical manipulations that can affect the final output. Often it is difficult to verify if they are being done correctly. Furthermore, the user must understand what exposure or toxicity parameters are hardwired into the software and compare those with any required state-specific parameters.

OTHER CONSIDERATIONS FOR OVERSEAS APPLICATIONS

HAS THE TPHCWG METHODOLOGY BEEN ACCEPTED BY OVERSEAS REGULATORS?

The international community looks to North America and Europe for many of their environmental regulations. This is evident from the review of existing regulations that was presented previously in this manual. As such, it is expected that the risk-based approach that has been developed by PERF will have applications outside the borders of the United States.

More specifically, the risk-based approach for managing complex hydrocarbons, as developed by the TPHCWG and later modified by PERF, has been presented to international regulators from Nigeria. In response to this presentation, the environmental regulators of Nigeria have agreed to consider the use of the methodology for managing onshore facilities in lieu of their proposed TPH standard of 50 mg/kg for soil.

WHAT SPECIAL FACTORS SHOULD BE CONSIDERED WHEN PREPARING TO APPLY THE TPHCWG METHODOLOGY TO AN INTERNATIONAL E&P SITE?

The TPH risk-based methodology is valid for application to international E&P sites; however, some of the data and assumptions may require some modifications. For example, it is unlikely that the default risk assumptions that are used in the United States will be directly applicable to situations in developing countries. Soil and water

Data and default assumptions used in risk-based assessments of TPH should be carefully reviewed prior to their international application.

ingestion rates, to name two parameters, will no doubt be different in agriculturally based countries with no public water supplies. As such, the E&P manager will need to gain a thorough understanding of the regulatory environment and needs of the indigenous populations to assist him or her in the development of a site conceptual model that is representative of the region in which he or she is operating. The potential future land uses at an international site will also be driven by the needs of the local population as well as the national culture. Defining the land uses so that they are acceptable to all local stakeholders must also be carefully done.

PART VI

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APPENDIX A

E&P WASTES:

REGULATORY STATUS

In 1978, EPA proposed hazardous waste management standards that included reduced requirements for several large volume wastes. Subsequently, in 1980, Congress exempted these wastes from the Resource Conservation and Recovery Act (RCRA) Subtitle C hazardous waste regulations pending a study and regulatory determinations by EPA. In 1988, EPA issued a regulatory determination stating that the control of E&P wastes under RCRA Subtitle C regulations was not warranted. This RCRA Subtitle C exemption, however, does not preclude these wastes from control under other Federal regulations (e.g., the RCRA Subtitle D Guidelines, the Clean Air Act, the Clean Water Act, the Safe Drinking Water Act, and the Oil Pollution Act of 1990), or under State hazardous or non-hazardous regulations. In addition, releases of E&P wastes may be subject to EPA enforcement under Section 7003 and State or citizen suit enforcement under RCRA Section 7002 where the release may present an imminent hazard to human health and the environment.

SUMMARY OF E&P WASTES

E&P wastes are generated by the primary field operations at an oil or gas exploration and production site. Primary field operations include exploration, development, and the primary, secondary, and tertiary production of oil or gas. More specifically, at an exploration and production site, primary field operations include activities occurring before the point where the oil and natural gas are transferred from an individual field facility or a centrally located facility:

- In the case of oil production, to a trucking company or pipeline for transport to a refinery or refiner
- In the case of natural gas production, to a pipeline for transportation to natural gas processing, treatment, or market

Examples of primary field operations include:

- Seismic surveying to detect potential oil and gas reservoirs
- Drilling and working over wells
- Lifting oil, gas, and water production from the reservoir to the surface with flowing, pumped, or gas-lifted wells

- Movement of produced fluids from the well to tank batteries and other facilities associated with a specific well or wells
- Oil, gas, and water separation
- De-emulsification of oil-water mixtures
- Liquid storage at tank batteries
- Dehydration and sweetening of natural gas
- Gas compression
- Measurement of gas and liquids
- Disposal of produced salt water
- Re-injection of water, gas, or other substances for secondary recovery

Natural gas often requires processing to recover natural gas liquids, as well as treatment to remove water, hydrogen sulfide, carbon dioxide, or other impurities, prior to being delivered to transmission pipelines for transportation to final end-users. Wastes generated at gas gathering pipeline facilities and associated gas treatment plants and gas processing plants are considered to be E&P wastes regardless of their location with respect to the primary field operations.

Some examples of the wastes that are produced during oil and gas exploration and production as abstracted from a previous API report [API, 1997] are provided in Table A-1.

STATUS OF E&P WASTES UNDER RCRA

E&P EXEMPTION FROM FEDERAL RCRA SUBTITLE C REQUIREMENTS

E&P wastes that are exempt from RCRA Subtitle C requirements include produced water, drilling fluids, and "other wastes associated with the exploration, development, or production of crude oil or natural gas". According to the legislative history, the term "other wastes associated" specifically includes waste materials intrinsically derived from primary field operations associated with the exploration, development, or production of crude oil and natural gas. Examples of associated wastes include crude oil tank bottoms and oil-impacted soil. The phrase "intrinsically derived from the primary field operations" is intended to distinguish exploration, development, and production operations from transportation and manufacturing operations. These wastes are commonly referred to as "exempt wastes." (This discussion covers Federal law only. States and local E&P waste rules may be more stringent or include additional requirements.)

The following questions can be used to determine if an E&P waste is exempt or non-exempt from RCRA Subtitle C Regulations:

- (1) *Has the waste come from down-hole, i.e., was it brought to the surface during oil and gas E&P operations?*
- (2) *Has the waste otherwise been generated by contact with the oil and gas production stream during the removal of produced water or other contaminants from the product?*

If the answer to either of these questions is yes, then the waste is most likely considered exempt from RCRA Subtitle C regulations [U.S. EPA, 1995].

TABLE A-1. SUMMARY OF WASTES FROM OIL AND GAS EXPLORATION

Exploration	Drilling	Well Completion and Workover	Field Production	Gas Plant Operations
<ul style="list-style-type: none"> • Filters • Hydraulic Fluid • Mud/Cuttings from Shot Holes • Contaminated Soil • Solvents (Petroleum Naphtha) • Rig Washdown Water 	<ul style="list-style-type: none"> • Cement Returns • Completion Workover and Well Treatment Fluids • Drill Cuttings • Drilling Fluids • Filters • Hydraulic Fluid • Produced Sand • Produced Water • Contaminated Soil • Solvents • Hydrocarbon Spill Cleanup Waste • Rig Washdown Water 	<ul style="list-style-type: none"> • Cement Return • Completion Workover and Well Treatment Fluids • Pit Sludges • Produced Sand • Produced Water • Waste Crude Oil/Condensate • Filters • Drill Cuttings • Drilling Fluids • Hydraulic Fluid • Naturally Occurring Radioactive Material • Packing Fluids • Paraffin • Contaminated Soil • Solvents • Hydrocarbon Spill Cleanup Waste • Rig Washdown Water 	<ul style="list-style-type: none"> • Boiler Blowdown • Catalyst • Process Equipment Cleaning Wastes • Completion Workover and Well Treatment Fluids • Cooling Tower Blowdown • Waste Crude Oil/Condensate • Filters • Hydraulic Fluid • Metallic Liquid Mercury • Mercury Solids • Naturally Occurring Radioactive Material • Naturally Occurring Radioactive Material • Pit Sludges • Produced Sand • Produced Water • H₂S Scrubber Liquid • Contaminated Soil • Solvents • Sulfur Dioxide Liquor • Sweetening/Dehydration Solids and Liquids • Tank Bottoms • Packing Fluids • Paraffin • Piggings Wastes • Pipeline/Equipment Hydrates • Rig Washdown Water • Hydrocarbon Spill Clean-up Wastes 	<ul style="list-style-type: none"> • Boiler Blowdown • Catalyst • Process Equipment Cleaning Wastes • Cooling Tower Blowdown • Waste Crude Oil/Condensate • Filters • Hydraulic Fluid • Metallic Liquid Mercury • Mercury Solids • Naturally Occurring Radioactive Material • Piggings Wastes • Pipeline/Equipment Hydrates and Scale • Pit Sludges • Produced Sand • Produced Water • Hydrogen Sulfide Scrubber Liquid • Contaminated Soil • Solvents • Hydrocarbon Spill clean-up Waste • Sulfur Dioxide Liquor • Sweetening /Dehydration Liquids and Solids

In 1987, the U.S. EPA provided a report to Congress that contained a list of E&P wastes that were determined to be either exempt or nonexempt wastes [U.S. EPA, 1987]. This list, which was later clarified [U.S. EPA, 1993], is provided in Table A-2. EPA stated that the list of wastes in Table A-2 represent examples of exempt and non-exempt wastes and should not be considered comprehensive. They also noted that the list applied only to those wastes generated by E&P operations; similar wastes generated by activities other than E&P operations are not covered by the exemption. Of particular relevance to the risk-based management of E&P sites is the listing of hydrocarbon-bearing soil as an exempt waste.

REGULATION OF MIXTURES OF EXEMPT AND NON-EXEMPT WASTES

The mixing of exempt and non-exempt wastes is not precluded by the regulations but should be done with care. If the non-exempt waste is a listed or characteristic hazardous waste, the resulting mixture might become a non-exempt waste and require management under RCRA Subtitle C regulations. In addition, mixing a characteristic hazardous waste with a non-hazardous or exempt waste for the purpose of rendering the hazardous waste non-hazardous or less hazardous might be considered a treatment process subject to applicable RCRA Subtitle C hazardous waste regulation and permitting requirements. On the other hand, mixing a non-hazardous, non-exempt waste with an exempt waste would not be subject to Subtitle C regulations (i.e., the mixture would be exempt). This is discussed in more detail below.

Determining the regulatory status of a mixture of an exempt and non-exempt waste requires an understanding of the nature of the wastes prior to mixing and, in some cases, might require chemical analysis of the mixture. The EPA has established a logic flowchart to assist in making these determinations. Although conducting a formal, detailed assessment of wastes handled should be completed to ensure proper handling, the statements below can be used as a general guideline:

- A mixture of an exempt waste with another exempt waste remains exempt.
- A mixture of a non-hazardous waste (exempt or non-exempt) with an exempt waste results in a mixture that is also exempt.
- If, after mixing a non-exempt characteristic hazardous waste with an exempt waste, the resulting mixture exhibits any of the same hazardous characteristics as the hazardous waste (i.e., ignitability, corrosivity, reactivity, or toxicity), the mixture is a non-exempt hazardous waste.

TABLE A-2. LIST OF EXEMPT AND NON-EXEMPT E&P WASTES [U.S. EPA, 1993]

Exempt Wastes	Non-Exempt Wastes
<ul style="list-style-type: none"> • Produced water • Drilling fluids • Drill cuttings • Rigwash • Well completion, treatment, and stimulation fluids • Basic sediment, water, and other tank bottoms from storage facilities holding product and exempt waste • Accumulated materials such as hydrocarbons, solids, sands, and emulsion from production separators, fluid treating vessels, and production impoundments • Pit sludges and contaminated bottoms from storage or disposal of exempt wastes • Gas plant dehydration wastes including glycol-based compounds, glycol filters, and filter media, backwash, and molecular sieves • Workover wastes • Cooling tower blowdown • Gas plant sweetening wastes for sulfur removal including amines, amine filters, amine filter media, backwash, precipitated amine sludge, iron sponge, and hydrogen sulfide scrubber liquid and sludge • Spent filters, filter media, and backwash (assuming the filter itself is not hazardous and the residue in it is from an exempt waste stream) • Pipe scale, hydrocarbon solids, hydrates, and other deposits removed from piping and equipment prior to transportation • Produced sand • Packing fluids • Hydrocarbon-bearing soil • Pigging wastes from gathering lines • Wastes from subsurface gas storage and retrieval • Constituents removed from produced water before it is reinjected or otherwise disposed of • Liquid hydrocarbons removed from the production stream but not from oil refining • Gases from the production stream such as hydrogen sulfide and carbon dioxide and volatilized hydrocarbons • Materials ejected from a production well during blowdown • Waste crude oil from primary field operations • Light organics volatilized from exempt wastes in reserve pits, impoundments, or production equipment 	<ul style="list-style-type: none"> • Unused fracturing fluids or acids • Gas plant cooling tower cleaning wastes • Painting wastes • Waste solvents • Oil and gas service company wastes such as empty drums, drum rinsate, sandblast media, painting wastes, spent solvents, spilled chemicals, and waste acids • Vacuum truck and drum rinsate from trucks and drums transporting or containing non-exempt waste • Refinery wastes • Liquid and solid wastes generated by crude oil and tank bottom reclaimers* • Used equipment lubricating oils • Waste compressor oil, filters, and blowdown • Used hydraulic fluids • Waste in transportation pipelines and related pits • Caustic or acid cleaners • Boiler cleaning wastes • Boiler refractory bricks • Boiler scrubber fluids, sludges, and ash • Incinerator ash • Laboratory wastes • Sanitary wastes • Pesticide wastes • Radioactive tracer wastes • Drums, insulation, and miscellaneous solids <p>* Although non-E&P wastes generated from crude oil and tank bottom reclamation operations (e.g., waste equipment cleaning solvent) are non-exempt, residuals derived from exempt wastes (e.g., produced water separated from tank bottoms) are exempt</p>

- If, after mixing a non-exempt characteristic hazardous waste with an exempt waste, the resulting mixture does not exhibit any of the same characteristics as the hazardous waste, the mixture is exempt. Even if the mixture exhibits some other characteristics of a hazardous waste, it is still exempt.
- Generally, if a listed hazardous waste (i.e., a waste listed as hazardous in the Code of Federal Regulations under Subpart D of 40 *CFR* Part 261) is mixed with an exempt waste, regardless of the proportions, the mixture is a non-exempt hazardous waste.

Due to the complexity of the waste characteristics and the environmental regulations, it should be understood that these guidelines only provide a broad overview of possible waste management strategies. Before a final strategy is implemented for a given site, the site manager should consult the governing regulatory agency and/or an environmental expert in this area.

APPENDIX B

EQUATIONS FOR CALCULATION OF RISK-BASED SCREENING LEVELS FOR SOIL[†]

- Direct Ingestion and Dermal Contact with Surface Soil
- Inhalation of Volatiles and Particulates from Surface Soil
- Leaching to Groundwater
- Volatilization to Outdoor Air

[†] Many of the EPA default values used for the parameters in these equations are listed on page 31 of this document. Those that are not provided are either chemical- or site-specific.

EQUATION FOR SOIL RBSL: DIRECT INGESTION AND DERMAL CONTACT WITH SURFACE SOIL

$$\text{RBSL}_{\text{ss}} \left[\frac{\mu\text{g}}{\text{kg-soil}} \right] = \frac{\text{THQ} \times \text{BW} \times \text{AT}_n \times 365 \frac{\text{days}}{\text{year}}}{\text{EF} \times \text{ED} \left[\frac{10^{-6} \frac{\text{kg}}{\text{mg}} \times (\text{IR}_{\text{soil}} \times \text{RAF}_o + \text{SA} \times \text{M} \times \text{RAF}_d)}{\text{RfD}_o} \right]}$$

where:

- THQ = Target hazard quotient for individual constituents [unitless]
- BW = Body weight [kg]
- AT_n = Averaging time for non-carcinogens [years]
- EF = Exposure frequency [days/year]
- ED = Exposure duration [years]
- IR_{soil} = Soil ingestion rate [mg/day]
- RfD_o = Oral chronic reference dose [mg/kg-day]
- RAF_d = Dermal relative absorption factor [unitless]
- RAF_o = Oral relative absorption factor [unitless]
- SA = Skin surface area [cm²/day]
- M = Soil to skin adherence factor [mg/cm²]

**EQUATION FOR SOIL RBSL: INHALATION OF VOLATILES
AND PARTICULATES FROM SURFACE SOIL**

$$\text{RBSL}_{\text{ss}} \left[\frac{\mu\text{g}}{\text{kg-soil}} \right] = \frac{\text{THQ} \times \text{BW} \times \text{AT}_n \times 365 \frac{\text{days}}{\text{year}}}{\text{EF} \times \text{ED} \left[\frac{10^{-6} \frac{\text{kg}}{\text{mg}} \times (\text{IR}_{\text{air}} \times (\text{VF}_{\text{ss}} + \text{VF}_{\text{p}}))}{\text{RfD}_i} \right]}$$

where:

- THQ = Target hazard quotient for individual constituents [unitless]
- BW = Body weight [kg]
- AT_n = Averaging time for non-carcinogens [years]
- EF = Exposure frequency [days/year]
- ED = Exposure duration [years]
- IR_{air} = Air inhalation rate [m³/day]
- RfD_i = Inhalation chronic reference dose [mg/kg-day]
- VF_p = Surficial soils to ambient air partition factor [particulates]
- VF_{ss} = Surficial soils to ambient air partition factor [vapors]

EQUATION FOR SOIL RBSL: LEACHING TO GROUNDWATER

Groundwater RBSL

$$\text{RBSL}_{\text{gw}} \left[\frac{\text{mg}}{\text{L-H}_2\text{O}} \right] = \frac{\text{THQ} \times \text{RfD}_o \times \text{BW} \times \text{AT}_n \times 365 \frac{\text{days}}{\text{year}}}{\text{IR}_w \times \text{EF} \times \text{ED}}$$

where:

- THQ = Target hazard quotient for individual constituents [unitless]
- RfD_o = Oral chronic reference dose [mg/kg-day]
- BW = Body weight [kg]
- AT_n = Averaging time for non-carcinogens [years]
- IR_w = Daily water ingestion rate [L/day]
- EF = Exposure frequency [days/year]
- ED = Exposure duration [years]

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Soil RBSL Based on Groundwater RBSL

$$\text{RBSL}_s [\text{mg/kg-soil}] = \frac{\text{RBSL}_{\text{gw}} [\text{mg/L-H}_2\text{O}]}{\text{LF}_{\text{sw}}}$$

$$\text{LF}_{\text{sw}} = \frac{\rho_s}{[\theta_{\text{ws}} + k_s \rho_s + H\theta_{\text{as}}] \left(1 + \frac{U_{\text{gw}} \delta_{\text{gw}}}{\text{IW}} \right)}$$

where:

- LF_{sw} = leaching factor [mg/L-H₂O/mg/kg-soil]
- U_{gw} = groundwater Darcy velocity [cm/y]
- *_{gw} = groundwater mixing zone thickness [cm]
- I = infiltration rate of water through soil [cm/y]
- W = width of source area parallel to groundwater flow direction [cm]
- Δ_s = soil bulk density [g/cm³]
- H = Henry's Law constant [cm³/cm³]
- 1_{as} = volumetric air content in vadose-zone soils [cm³/cm³]
- 1_{ws} = volumetric water content in vadose-zone soils [cm³/cm³]
- K_s = soil-water sorption coefficient [(g/g-soil)/(g/cm³-H₂O)]

EQUATION FOR SOIL RBSL: VOLATILIZATION TO OUTDOOR AIR

Outdoor Air RBSL

$$\text{RBSL}_{\text{air}} \left[\frac{\mu\text{g}}{\text{m}^3 - \text{air}} \right] = \frac{\text{THQ} \times \text{RfD}_i \times \text{BW} \times \text{AT}_n \times 365 \frac{\text{days}}{\text{year}} \times 10^3 \frac{\mu\text{g}}{\text{mg}}}{\text{IR}_{\text{air-in}} \times \text{EF} \times \text{ED}}$$

where:

- THQ = Target hazard quotient for individual constituents [unitless]
- RfD_i = Inhalation chronic reference dose [mg/kg-day]
- BW = Body weight [kg]
- AT_n = Averaging time for non-carcinogens [years]
- IR_{air-in} = Daily air inhalation rate [m³/day]
- EF = Exposure frequency [days/year]
- ED = Exposure duration [years]

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Soil RBSL Based on Outdoor Air RBSL

$$\text{RBSL}_{\text{svout}} \left[\frac{\text{mg}}{\text{kg} - \text{soil}} \right] = \frac{\text{RBSL}_{\text{air}} \left[\frac{\text{mg}}{\text{m}^3 - \text{air}} \right]}{\text{VF}_{\text{samb}}}$$

$$\text{VF}_{\text{samb}} = \frac{\text{H}\rho_s \times 10^3}{[\theta_{\text{ws}} + k_s \rho_s + \text{H}\theta_{\text{as}}] \left(1 + \frac{U_{\text{air}} \delta_{\text{air}} L_s}{D_s^{\text{eff}} W} \right)}$$

where:

- VF_{samb} = volatilization factor [mg/m³-air/mg/kg soil]
- U_{air} = wind speed above ground surface in ambient mixing zone [cm/s]
- *_{air} = ambient air mixing zone height [cm]
- L_s = depth to subsurface soil sources [cm]
- D_s^{eff} = effective diffusion coefficient between groundwater and soil surface [cm²/s]
- W = width of source area parallel to wind direction [cm]
- Δ_s = soil bulk density [g/cm³]
- H = Henry's Law constant [cm³/cm³]
- l_{as} = volumetric air content in vadose-zone soils [cm³/cm³]
- l_{ws} = volumetric water content in vadose-zone soils [cm³/cm³]
- K_s = soil-water sorption coefficient [(g/g-soil)/(g/cm³-H₂O)]

APPENDIX C

CONSIDERATION OF HYDROCARBON-SATURATED SOIL CONDITIONS DURING CALCULATION OF RBSLS

As part of the RBSL calculations, the concentrations of the individual carbon number fractions are compared to saturated soil concentrations or C_{SAT} . C_{SAT} is the soil concentration at which the soil pore water and pore vapor become saturated with the hydrocarbon fraction. It is back-calculated using partition coefficients and the maximum water solubility and vapor phase concentrations for each hydrocarbon fraction as shown below [TPHCWG, 1997a]:

$$C_{SAT} = \frac{S}{\rho_s} [H\Theta_{as} + \Theta_{ws} + K_s \rho_s] \frac{g}{g - soil}$$

where:

- S = pure component solubility (g/cm³-H₂O)
- ρ_s = soil bulk density [g/cm³]
- H = Henry's Law constant [cm³/cm³]
- Θ_{as} = volumetric air content in vadose-zone soils [cm³/cm³]
- Θ_{ws} = volumetric water content in vadose-zone soils [cm³/cm³]
- K_s = soil-water sorption coefficient [(g/g-soil)/(g/cm³-H₂O)]

(This equation for C_{SAT} is identical to that used in the screening level transport models of the ASTM Procedure E-1739-95. The parameters, ρ_s , Θ_{as} , and Θ_{ws} , are soil- and site-specific; K_s can be determined from the organic carbon partition coefficient, K_{oc} . Methods to estimate K_{oc} as well as S and H have been published by the TPHCWG [TPHCWG, 1997a].) Since C_{SAT} represents the worst case situation for contaminant leaching and volatilization, the smaller of the C_{SAT} concentration and the calculated concentration of the hydrocarbon fraction (i.e., $F_i \cdot C_{TOT}$) is used in the calculation. Concentrations greater than C_{SAT} would not result in an increase in the contaminant concentrations in the pore water or pore vapor and, hence, would not increase the risk associated with the presence of the TPH. However, these concentrations would increase the calculated hazard index for the total TPH which would result in the calculation of a lower soil clean-up goal for TPH without achieving any additional reduction in risk.

For more details on soil saturation conditions and their impact on risk management decisions associated with TPH, the reader should consult TPHCWG, 1997a.

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