
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

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



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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

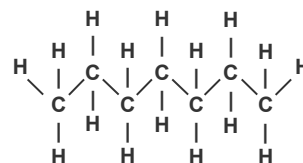
Figure 2 describes the major classes of petroleum hydrocarbons that are present in crude oil. The primary saturated and unsaturated hydrocarbons consist of n-alkanes, isoalkanes, cycloalkanes, and the mono-,

Chapter Overview:

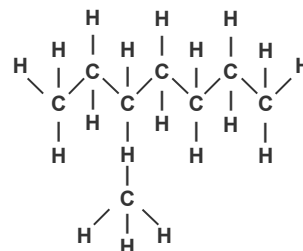
- Presents chemical, physical and toxicological characteristics
- Compares and contrasts characteristics of different materials

Saturates: (alkanes or paraffins)

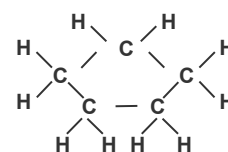
n-Alkane:



Isoalkane:

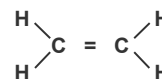


Cycloalkane:

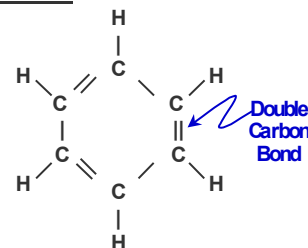


Unsaturates:

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

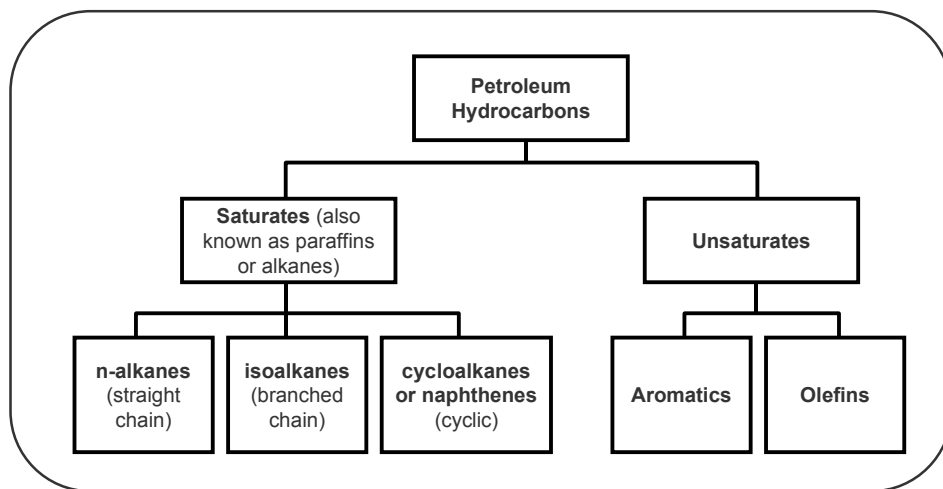
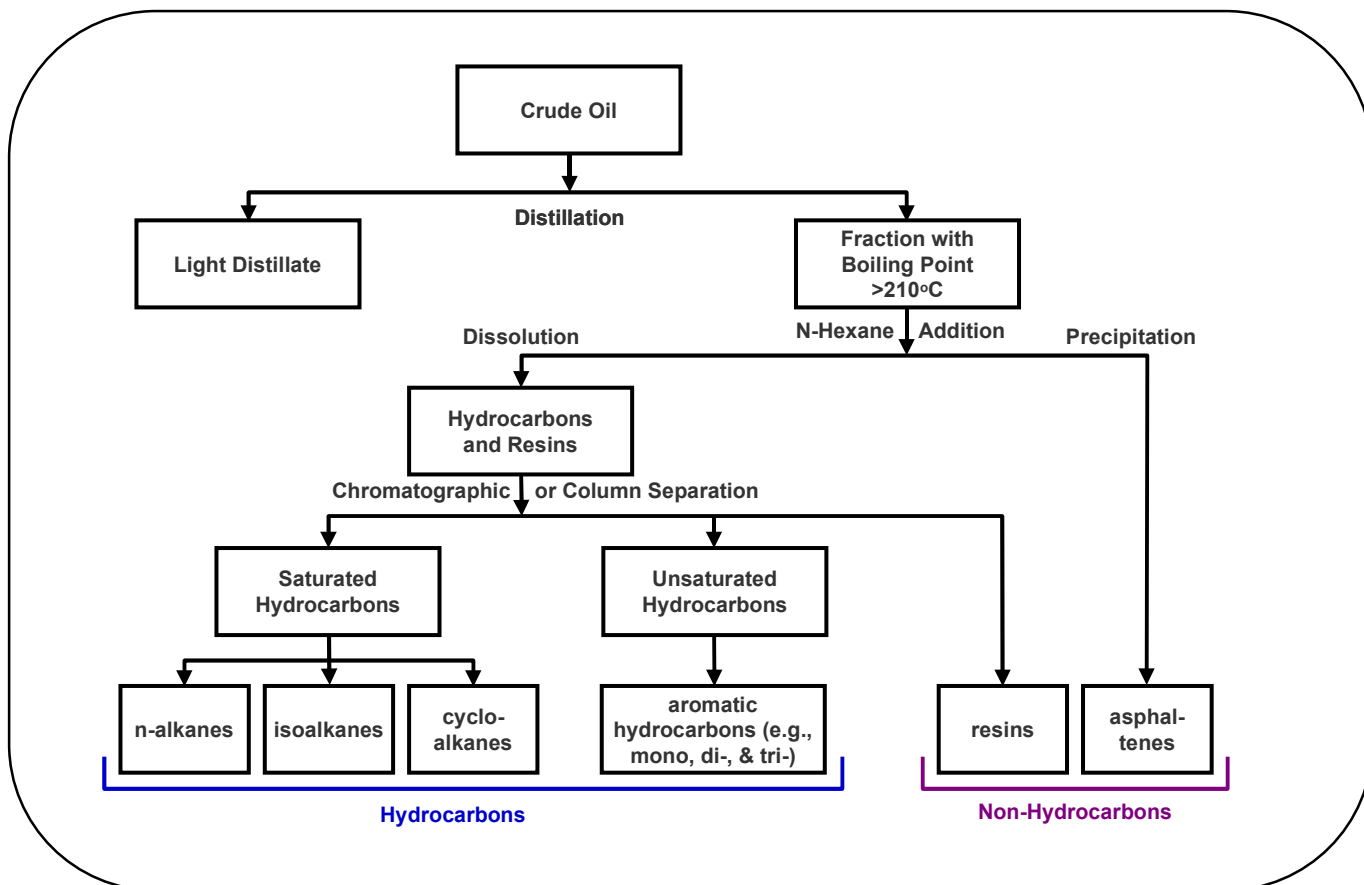


FIGURE 2. MAIN GROUPS OF CHEMICAL COMPOUNDS IN CRUDE OIL



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

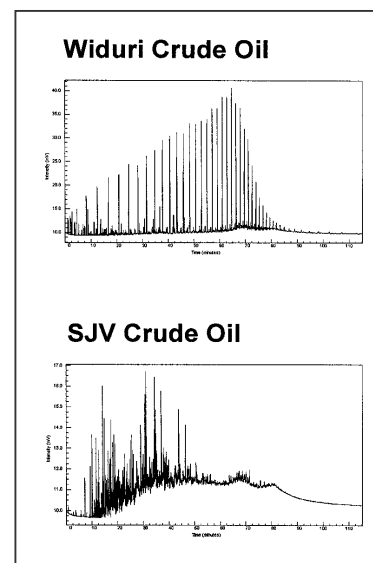
Composition of normal crude oil is bounded as follows:

- 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)

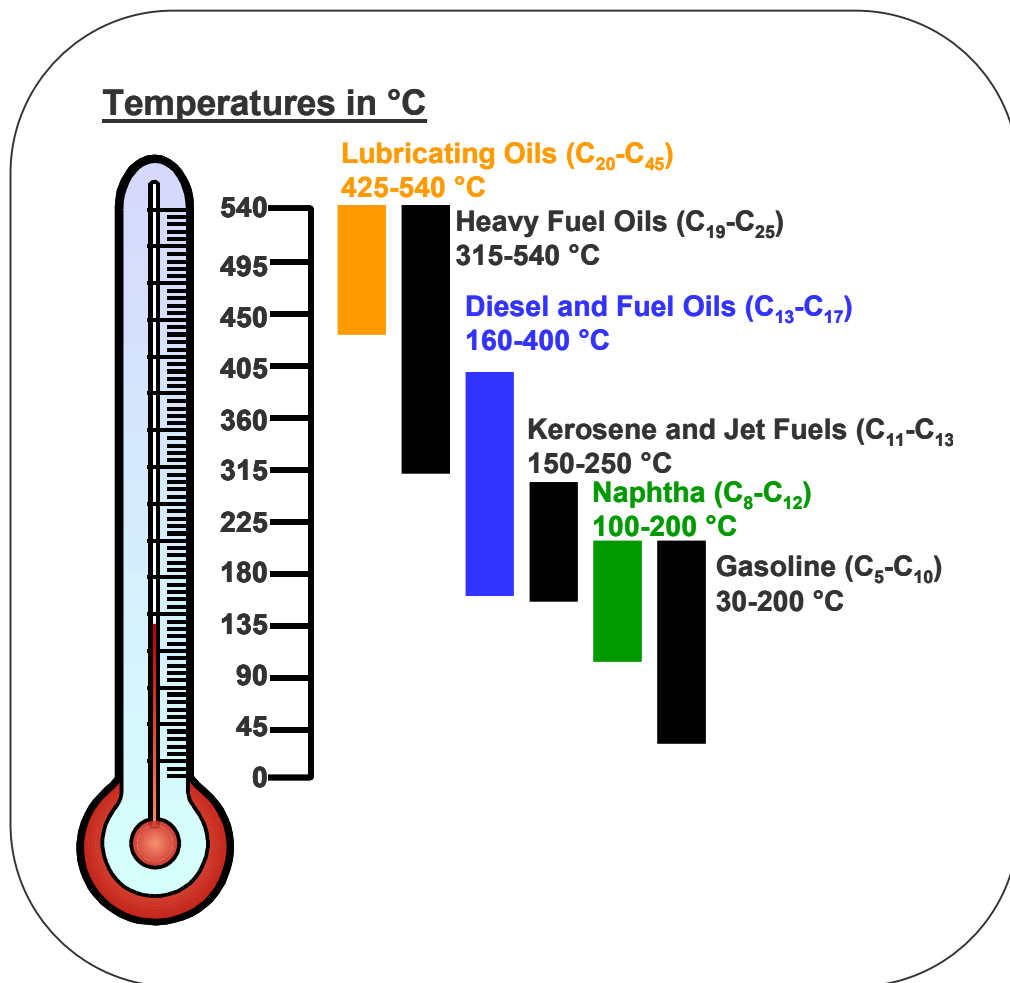
Blending agents and additives are also added to refined products. Examples of these include:

- 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:

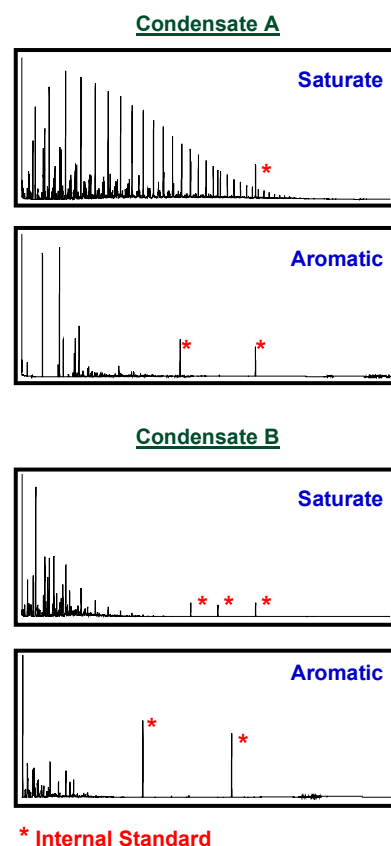
- Major chemical components are the straight-chained and branched saturated and unsaturated hydrocarbons.
- Benzene concentrations ranged from approximately 0.15 to 3.6% by weight.
- Only three of the seven carcinogenic PAHs were detected in condensates (benzo(b)fluoranthene, chrysene, and benzo(a)-anthracene). 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



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)