

# Frequently Asked Questions About TPH Analytical Methods for Crude Oil

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

*TPH measurements of several natural materials yield significant TPH concentrations:*



## 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  $\leq 10,000$  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. Recent research initiatives have established a more consistent technical approach for the management of petroleum hydrocarbons that emphasizes the protection of human health and determined that 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***

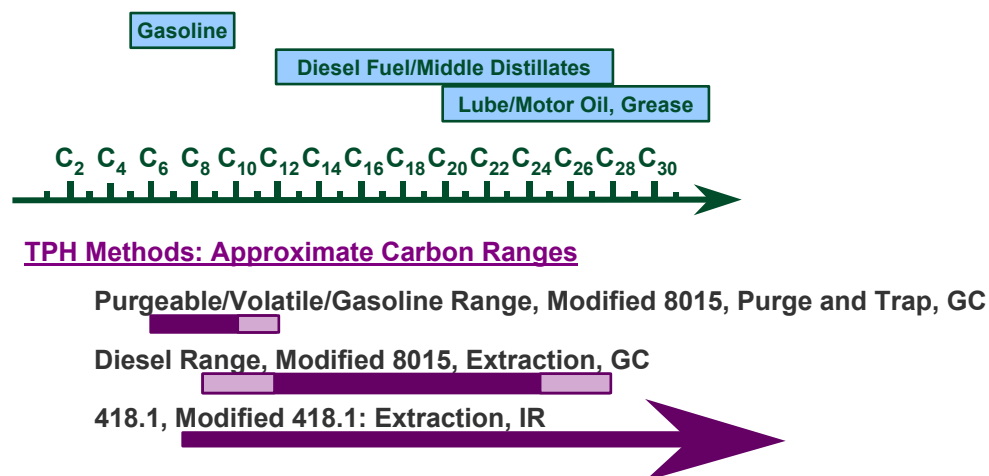
Some of the more common methods for the analysis of TPH include: (1) Method 418.1 or Modified 418.1, (2) Method 413.1 for oil and grease, (3) Modified 8015M for Diesel-Range Organics (DRO) and (4) Modified 8015M for Gasoline-Range Organics (GRO) [TPHCWG, 1998]. Method 418.1 consists of solvent extraction followed by treatment in a silica gel column and infrared spectroscopy; the modified 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 1 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., C<sub>6</sub> to C<sub>12</sub>) may report some of the hydrocarbons present in diesel fuel (i.e., C<sub>10</sub> to C<sub>28</sub>). 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., C<sub>8</sub> to C<sub>40</sub>). However, crude oil contains hydrocarbons with carbon numbers that range from C<sub>3</sub> to C<sub>45+</sub> and is not fully addressed even with the use of all three TPH methods.

FIGURE 1. CARBON NUMBER RANGES ADDRESSED BY TPH ANALYTICAL METHODS



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

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

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).

*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.*

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 guidance for the development of protective concentration levels of hydrocarbon mixtures [TNRCC, 2000].

### **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 [Rhodes, 2001]. 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, 1998].

### **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 ( $C_{35}$ ). 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.,  $C_{35+}$ ) 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  $C_{35}$ . This was done by modifying the gas chromatographic technique to quantify hydrocarbons up to  $C_{44}$ . Then the fraction  $>C_{44}$  can be determined by distillation or it can be estimated. The hydrocarbon fraction with carbon numbers greater than  $C_{44}$  (i.e.,  $C_{44+}$ ) 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 [Douglas et al., 2001]. First, the gas chromatography was enhanced to permit the fractionation and detection of hydrocarbons with carbon numbers as high as  $C_{44}$ .

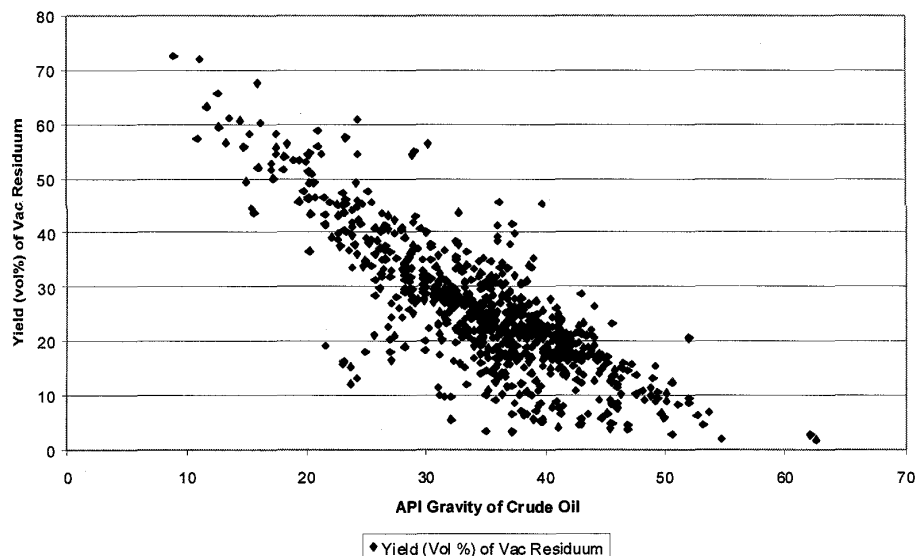
Next, PERF developed three approaches to determine the mass of hydrocarbon with carbon numbers greater than  $C_{44}$ . The most favored

*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°

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

**FIGURE 2. YIELD OF VACUUM RESIDUUM IN 800 CRUDE OILS PRODUCED IN THE UNITED STATES.**



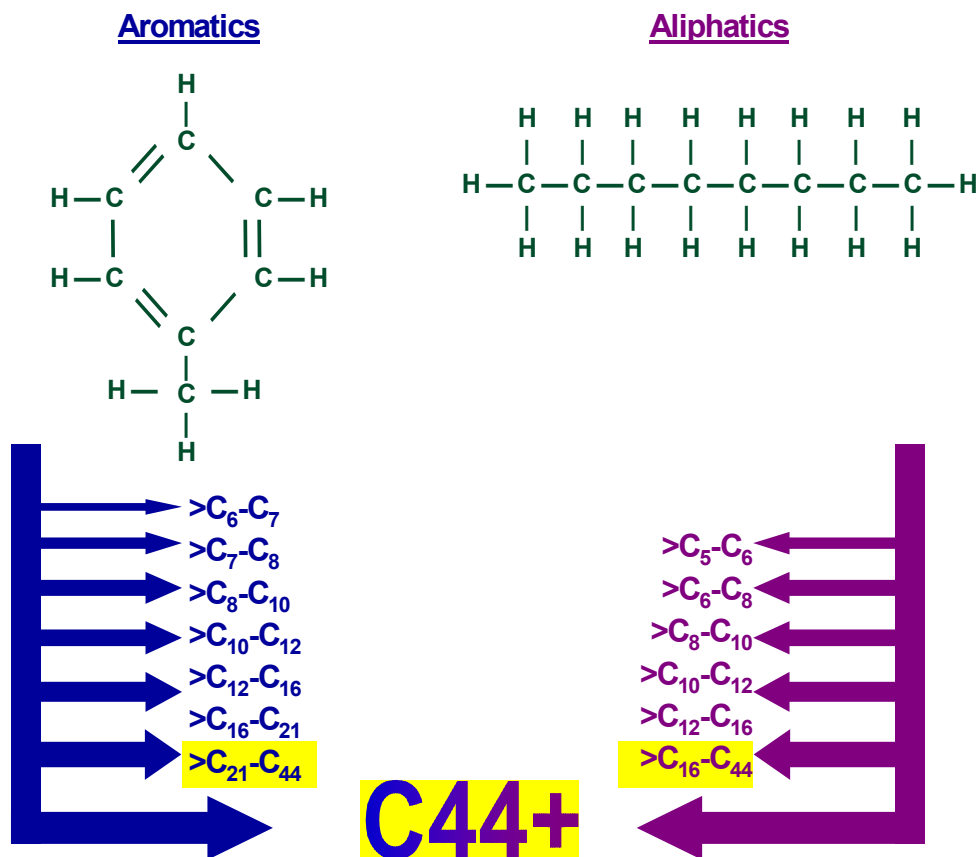
had been developed for crude oils between the yield of vacuum residuum and API gravity (Figure 2). This correlation was constructed using data from 800 crude oils in the United States [Coleman, et al., 1978]. It can be seen from Figure 2 that the yield (expressed in volume percent) of the vacuum residuum 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<sub>44+</sub> 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 3 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 are as follows:

- (1) The >C<sub>21</sub> to C<sub>35</sub> aromatic carbon number fraction was replaced by a >C<sub>21</sub> to C<sub>44</sub> carbon number fraction.
- (2) The >C<sub>16</sub> to C<sub>35</sub> aliphatic carbon number fraction was replaced by a >C<sub>16</sub> to C<sub>44</sub> carbon number fraction.
- (3) A C<sub>44+</sub> 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 C<sub>44+</sub> carbon number fraction.

**FIGURE 3. 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 3. Figure 4 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 C<sub>6</sub> to C<sub>44</sub>). 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 C<sub>6</sub> or greater than

*Distribution of hydrocarbons in 15 crude oils:*

- > 0 to 20%: <C<sub>6</sub>
- > 45 to 80%: C<sub>6</sub>-C<sub>44</sub>
- > 5 to 45%: >C<sub>44</sub>

C<sub>44</sub>. The data in Figure 4 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 C<sub>44+</sub> fraction for each of the 15 crude oils in Figure 4 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.

*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?**

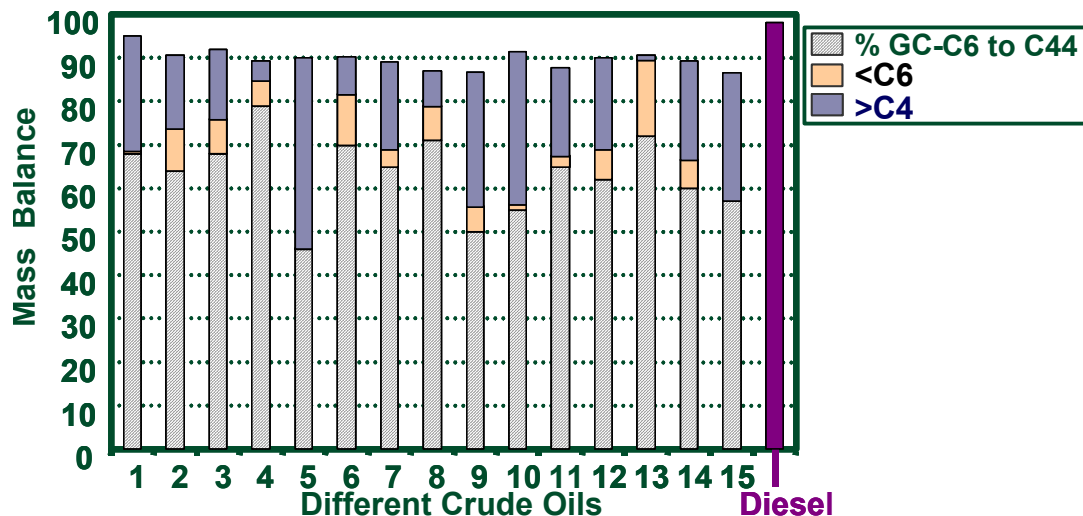
The use of conventional measures of bulk TPH is more than adequate for site management purposes providing that RBSLs have been determined for the specific hydrocarbon mixture at the site or for specific types of hydrocarbon mixtures. If it is suspected that multiple sources of different hydrocarbons 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.

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.

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

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. 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.

Figure 4. Categorization of Crude Oil Hydrocarbon into Carbon Number Fractions



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