TCEQ REGULATORY GUIDANCE
Remediation Division
RG-366/TRRP-27 ● January 2010

Development of Human Health PCLs for Total Petroleum Hydrocarbon Mixtures

Overview of this Document

Objectives: Describes the process to establish PCLs for total petroleum hydrocarbon mixtures

Audience: Environmental Professionals and the Regulated Community

References: The Texas Risk Reduction Program (TRRP) rule, together with conforming changes to related rules, is contained in 30TAC Chapter 350. The TRRP rule was initially published in the September 17, 1999 Texas Register (24 TexReg 7413-7944) and was amended in 2007 (effective March 19, 2007; 32 TexReg 1526-1579).

Find links for the TRRP rule and preamble, Tier 1 PCL tables, and other TRRP information at: www.tceq.state.tx.us/remediation/trrp/.

TRRP guidance documents undergo periodic revision and are subject to change. Referenced TRRP guidance documents may be in development. Links to current versions are at: www.tceq.state.tx.us/remediation/trrp/guidance.html.

Contact: TCEQ Remediation Division Technical Support Section - 512-239-2200, or techsup@tceq.state.tx.us

For mailing addresses, refer to: www.tceq.state.tx.us/about/directory/

Please note that the Texas Risk Reduction Program (TRRP) does not require that total petroleum hydrocarbon (TPH) be evaluated as a chemical of concern (COC) at an affected property. The COCs to be evaluated under the TRRP, including TPH, are decided by the person undertaking the corrective action in coordination with the applicable TCEQ program area. See TCEQ guidance document *Selecting Target COCs* (RG-366/TRRP-10) for further information. If you or the TCEQ program area determine that TPH is an applicable COC for an affected property, then this document should be followed to guide the development of appropriate PCLs for the TPH mixture(s) at the affected property.

TEXAS COMMISSION ON ENVIRONMENTAL QUALITY • PO BOX 13087 • AUSTIN, TX 78711-3087
The TCEQ is an equal opportunity employer. The agency does not allow discrimination on the basis of race, color, religion, national origin, sex, disability, age, sexual orientation, or veteran status. In compliance with the Americans with Disabilities Act, this document may be requested in alternate formats by contacting the TCEQ at 512-239-0028, fax 512-239-4488, or 1-800-RELAY-TX (TDD), or by writing PO Box 13087, Austin TX 78711-3087. We authorize you to use or reproduce any original material contained in this publication — that is, any material we did not obtain from other sources. Please acknowledge the TCEQ as your source. Printed on recycled paper.

Introduction

This guidance document describes a process to establish human health-based protective concentration levels (PCLs) for total petroleum hydrocarbons (TPH) in accordance with 30 TAC §350.76(g) of the Texas Risk Reduction Program (TRRP) rule. In many instances, the ability to establish PCLs for TPH will be a convenient tool to evaluate the protectiveness of a mass of petroleum hydrocarbons comprised of potentially hundreds of individual chemicals of concern (COCs), many of which lack the toxicity and chemical/physical property information needed for PCL development.

The development of TPH PCLs is dependent on the composition of the petroleum hydrocarbon product since different hydrocarbon products have different compositions. Therefore, the development of PCLs must be able to reflect the composition of the TPH in question. Contrasts in composition reflect differences in the relative percentages of toxic COCs and mobile COCs in the petroleum hydrocarbon product, both of which directly influence the derived PCL. The gross composition of a petroleum hydrocarbon product can be characterized by the chromatographic profiles or fingerprints generated using analytical gas chromatography techniques over a defined boiling point range. As shown in Figure 1, petroleum hydrocarbon products such as gasoline, diesel, motor oil, and jet fuel do not have the same compositions as reflected by the contrasts in the gas chromatographic fingerprints for the different products. Additionally, as illustrated by the gas chromatograms for the fresh and weathered gasoline in Figure 1, the products can change dramatically upon release into the environment due to environmental weathering and commingling with other petroleum hydrocarbon products (see the Product Composition and Weathering section at the end of this document for further discussion of this topic). Because the original petroleum hydrocarbon product may have weathered upon release to the environment or mixed with other petroleum hydrocarbon products such that the composition in the environmental medium may be dissimilar to the original product, the term “TPH mixture” will typically be used in following text in lieu of the term “petroleum hydrocarbon product.”

General Overview

To address issues of insufficient toxicity and chemical/physical property information for all potential COCs, the overwhelming number of COCs comprising petroleum hydrocarbon products, and the variability in the composition of the TPH, a process that closely follows the work of the

national Total Petroleum Hydrocarbon Criteria Working Group[1] is described in this guidance to establish TPH PCLs. A general overview of the process is illustrated in Figure 2 and is briefly summarized here.

When TPH is established as an applicable COC, samples from environmental media affected with TPH are collected during the affected property assessment for laboratory analysis using a gas chromatography method (TCEQ Method 1005). The analytical results are used to determine the extent of TPH-affected property, compositional distribution of the hydrocarbons in the TPH, and the magnitude of TPH concentrations in each affected environmental medium. Gas chromatography fingerprints for the different samples collected from the TPH source areas (that is areas of highest TPH concentrations in an environmental medium) are then compared to determine if the gross hydrocarbon composition of the TPH changes across the sampled area. When the gas chromatographic fingerprints indicate that different petroleum hydrocarbon products (Figure 1) were released in different areas of the affected property, then PCLs need to be established for each of those different TPH compositions for application in the respective source area for that petroleum hydrocarbon product and associated affected areas.

1 The TPH Criteria Working Group is a consortium of industry, academia, and governmental representatives who have worked since 1993 to develop evaluation methods for TPH. Information on the working group and publications can be found at http://www.aehs.com.

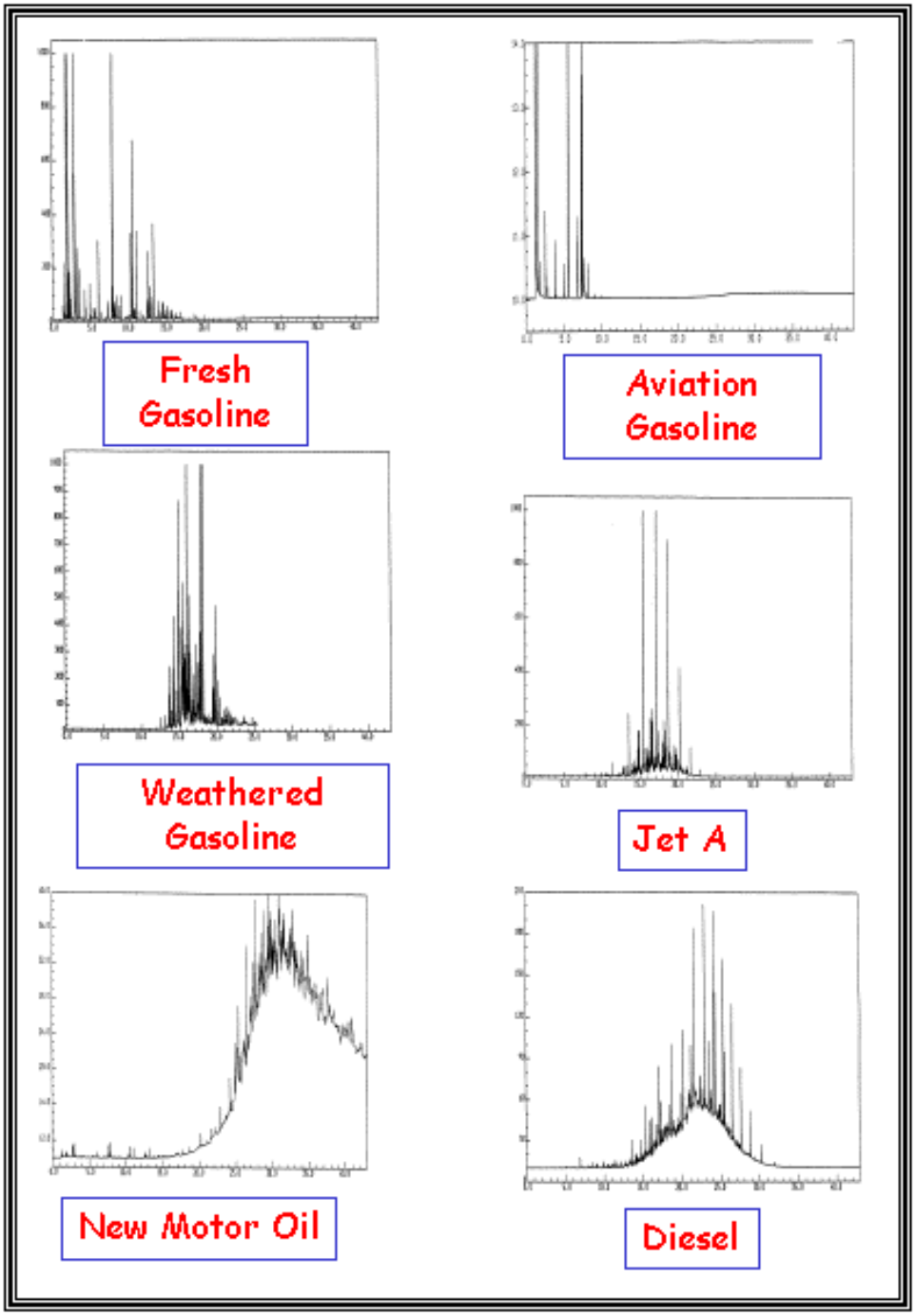

Figure 1. Chromatograms showing contrasts between the compositions of different petroleum hydrocarbon mixtures.

Based on chromatograms from TCEQ Method 1005 analysis, the sample with the highest concentration that is representative of the TPH in the source area(s) is selected and fractionated using a second laboratory analysis method (TCEQ Method 1006) into seven aliphatic boiling point ranges and six aromatic boiling point ranges of petroleum hydrocarbons (Figures 2 and 3). Subsequently, the concentration of each boiling point range is determined, and the mass fraction of each boiling point range

relative to the total mass of the TPH mixture is determined by dividing the concentration of each boiling point range by the total concentration of the TPH mixture. Tier 1, 2, or 3 PCLs are then derived for each boiling point range for each complete or reasonably anticipated to be completed exposure pathway as defined in 30 TAC §350.71(c) by using surrogate toxicity factors and surrogate chemical/physical properties (Tables 1 and 2) that represent the toxicity and mobility of the hydrocarbon compounds comprising that boiling point range. By following this procedure, each boiling point range is essentially treated as a COC. Once a PCL is established for each of the boiling point ranges comprising the TPH mixture for each exposure pathway, a PCL is then established for the TPH mixture itself (Figures 2 and 3). The PCL for the TPH mixture for a given exposure pathway is established by taking the inverse weighted average of the sum of the individual PCLs determined for each boiling point range for that same exposure pathway. The PCL for each boiling point range is weighted according to the mass of each specific boiling point range in the TPH mixture. The PCLs established for the TPH mixture for each exposure pathway for an affected environmental medium are then compared to determine the critical, that is, the lowest TPH PCL for that environmental medium. The critical TPH PCL for each environmental medium is then compared to the TPH concentrations within that environmental medium using the TPH results originally measured with TCEQ Method 1005 to determine where the critical PCLs are exceeded. The volume of the environmental medium with TPH concentrations in excess of the critical TPH PCL is defined as the PCL exceedance (PCLE) zone(s) and is to be addressed by a response action (Figure 2).

A detailed step-by-step explanation of the process is provided in the Procedural Steps to Establish PCLs for TPH Mixtures section of this document. In that more detailed explanation, screening procedures are introduced that may prevent the need to establish site-specific PCLs for the TPH at an affected property.

The TPH PCLs developed using this document provide an estimate of acceptable aggregate risk based on noncarcinogenic effects only. In addition to establishing PCLs for TPH, you typically will need to address individual COCs such as benzene, ethylbenzene, toluene, xylenes, polycyclic aromatic hydrocarbons, and other key petroleum hydrocarbon COCs, including metals in accordance with the requirements of the program area.

The process for setting PCLs for ecological receptors can be found in the TCEQ document *Guidance for Conducting Ecological Risk Assessments at Remediation Sites in Texas* (RG-263). In general, the process to calculate TPH PCLs for ecological receptors would be the same, but different surrogate toxicity factors would likely be assigned to the boiling point ranges. Therefore, consult with the TCEQ ecological risk assessment experts in the Technical Support Section for more information on ecological risk assessments.

TPH PCLs and the Tiered PCL Development Process

The TRRP establishes a three-tiered framework for PCL development. The development of TPH PCLs fits within that framework. PCLs for the aliphatic and aromatic boiling point ranges can be established under Tiers 1, 2, or 3 as referenced in Figure 2. Non-site-specific PCLs for the aliphatic and aromatic boiling point ranges are established under Tier 1. The Tier 1 PCLs for the aliphatic and aromatic boiling point ranges can be downloaded from the TRRP Web page and used to calculate Tier 1 PCLs for the TPH mixture as described above and later in this document. For information on the use of the Tier 1 TPH PCL Tables, see the TCEQ guidance document Proper Use of the Tier 1 PCL Tables (RG-366/TRRP-23). Alternatively, site-specific PCLs for the boiling point ranges, which consider characteristics of the affected property, lateral transport, and more appropriate natural attenuation factor models, may be established under Tiers 2 or 3 (see 30 TAC §350.75(a)-(d)). The Tier 2 or 3 PCLs for the different boiling point ranges can then be used to establish Tier 2 or 3 PCLs for the TPH mixture.

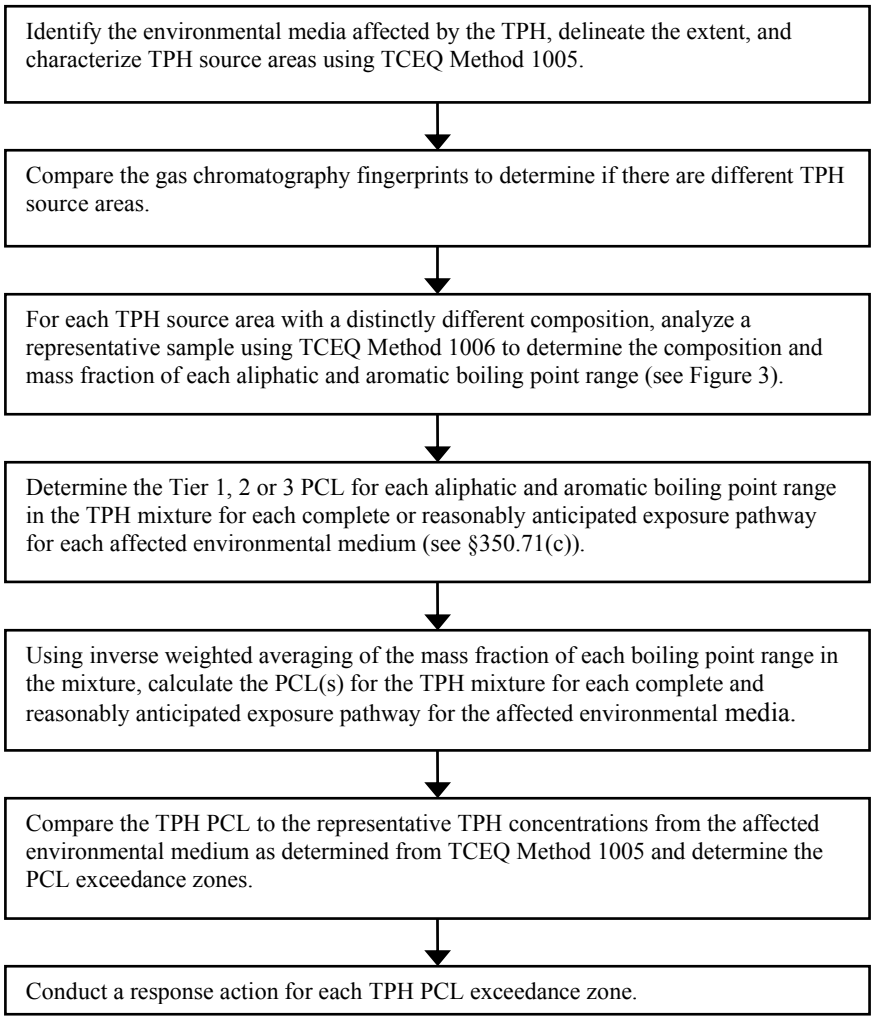

Figure 2. Overview of PCL Development Process.

Default versus Site-Specifically Determined TPH Mixture Compositions

As discussed previously, the composition of a petroleum hydrocarbon mixture is important to the development of PCLs. Therefore, the TCEQ may define, when appropriate and feasible, default compositions for various petroleum hydrocarbon mixtures in order to establish Tier 1 PCLs for the TPH mixtures (not just for the aliphatic and aromatic boiling point ranges). Providing PCLs for TPH mixtures may lessen the need to fractionate samples, which expedites the process and reduces costs. A default composition for transformer mineral oil has been adopted for the TRRP and Tier 1 PCLs for transformer mineral oil have been established accordingly. Default compositions for other TPH mixtures such as gasoline and diesel may be adopted by the TCEQ over time as sufficient information becomes available. When default compositions for TPH mixtures are adopted, you may use that default composition as long as it is used only for the same TPH mixture it is intended to represent. Laboratories can typically evaluate a gas chromatography fingerprint and determine the probable original petroleum hydrocarbon product unless it is mixed or so weathered so as to be unrecognizable. When a default composition for a TPH mixture has not been adopted for the particular TPH mixture under consideration, and the screening criteria discussed in Step 4 below are failed, then you will need to determine the site-specific TPH mixture composition using TCEQ Method 1006.

Analytical Methods for TPH

The measurement of TPH is a method-defined parameter, meaning that the composition and concentration of TPH is determined by the procedures followed in the analytical method. As introduced earlier, the TCEQ has developed two analytical methods for TPH. TCEQ Methods 1005 and 1006 should be used for determining concentrations of TPH, for establishing PCLs, and/or determining the composition of TPH for PCL development. If you wish to use an alternate method, then you must first submit a proposal to use an alternate method to the TCEQ and include in that proposal the data needed to validate the alternate method against TCEQ Method 1005 and 1006 as the reference methods. Once an alternate method has been approved for use under TRRP, the method, or reference to the method, will be placed on the TRRP Web page for others to use.

TCEQ Method 1005

Analytical results from TCEQ Method 1005 are primarily intended to be used to:

- determine the composition and concentration of the TPH at the affected property,
- identify source areas, and
- determine compliance with the established critical TPH PCLs.

Additionally, the results from the method may also be used as a screening tool to determine whether or not the development of PCLs for the TPH mixture is warranted as discussed under Steps 3 and 4 of the next section of this document.

TCEQ Method 1005 is an n-pentane extraction followed by a gas chromatography/flame ionization detection (GC/FID) analysis method that measures the concentration of hydrocarbons between n-C_6 and n-C_{35}. The laboratory includes a normal (n-) C_{12} alkane marker and an n-C_{28} alkane marker to aid the data user in evaluating the distribution of the hydrocarbons in the TPH based on the chromatographic profile. Results from TCEQ Method 1005 are reported as concentrations for the C6 -C12 boiling point range, the C_{12} -C_{28} boiling point range, the C_{28} -C_{35} boiling point range when applicable, and the sum of the concentration of the two or three boiling point range concentrations. TCEQ Method 1005 can be downloaded from www.tceq.state.tx.us/remediation/analysis.html.

TCEQ Method 1006

As discussed earlier, the analytical results from TCEQ Method 1006 are to be used to determine the concentrations of seven aliphatic boiling point ranges and six aromatic boiling point ranges of the TPH mixture in order to support development of TPH PCLs (Figure 3). The PCL for a TPH mixture is dependent upon the mass fraction represented by each boiling point range. Only the sample(s) to be used to represent the composition for the source area(s) need to be subjected to analysis using TCEQ Method 1006. Relative to TCEQ Method 1005, TCEQ Method 1006 is more expensive and therefore the agency is trying to minimize the use of the method to the extent possible.

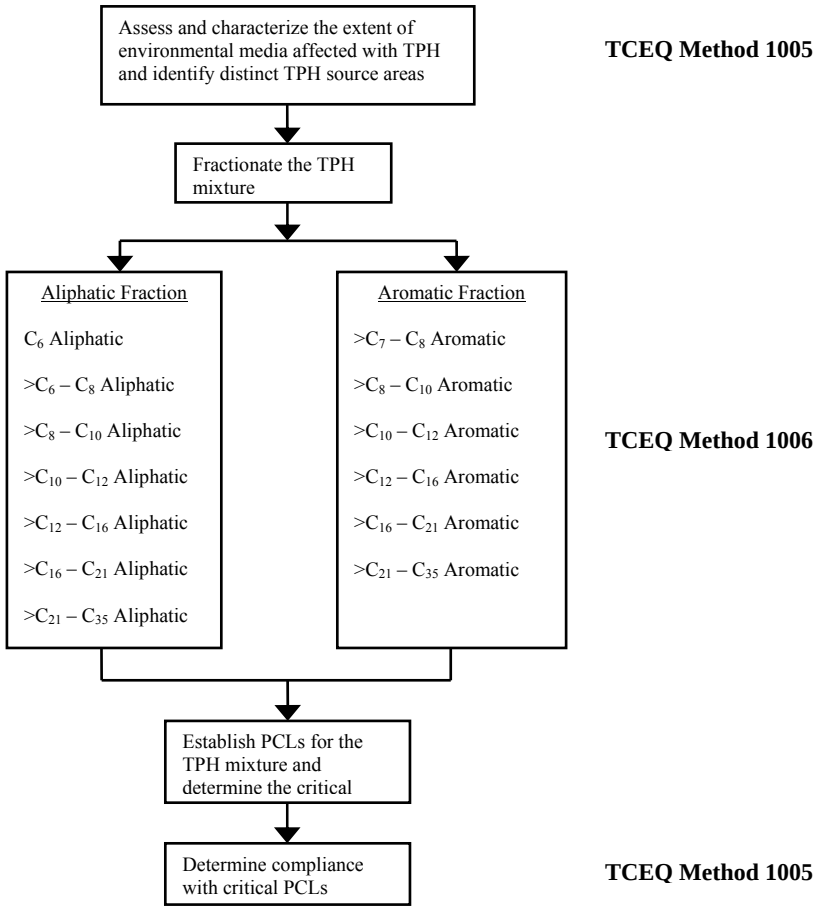

Figure 3. The applicability of TCEQ Methods 1005 and 1006 and boiling point ranges.

TCEQ Method 1006 uses a silica gel fractionation of the n-pentane extract to separate the TPH into the aliphatic hydrocarbon fraction and the aromatic hydrocarbon fraction and includes the analysis of each of these fractions by GC/FID. The GC/FID analysis of the fractions separates each fraction into discrete boiling point ranges based on normal alkane markers. TCEQ Method 1006 can be downloaded from www.tceq.state.tx.us/remediation/analysis.html.

Procedural Steps to Establish PCLs for TPH Mixtures

This section details the steps to establish PCLs for TPH mixtures. The section also discusses a screening step using the TCEQ Method 1005 data to avoid unwarranted development of PCLs for the TPH mixture. Figure 4 provides a decision framework that illustrates the process described in this section and identifies critical decision points. However, process Steps 8 and 9 are only cursorily addressed in Figure 4. A spreadsheet may be downloaded from the TRRP Web page that calculates the TPH mixture PCLs.

Step 1 Field Sampling

If TPH is an applicable COC, begin by collecting a sufficient number of samples for analysis using TCEQ Method 1005 to determine the concentrations and extent(s) of TPH in the environmental medium and to evaluate the number of source areas at the affected property to satisfy §350.51 requirements. Ensure that an adequate sample volume is collected from each sample point to allow for any subsequent analysis using TCEQ Method 1006 (see the documentation for TCEQ Method 1006 for specifics regarding required sample volume). As noted in Table 1 under footnote 4, the TCEQ Method 1005 and 1006 analyses can be truncated at C_{28} when there does not appear to be significant mass of hydrocarbons in the $>C_{28}$ boiling point range based on the TCEQ Method 1005 chromatogram, and it is anticipated that the TPH is composed of lighter hydrocarbons (for example, gasoline, diesel, and not transformer mineral oil or used motor oil).

Step 2 Source Area Identification

Use TCEQ Method 1005 data to identify TPH source areas. To determine the number of source areas of TPH and the volume of environmental media impacted by those sources, collect samples from the suspected source areas for TCEQ Method 1005 analysis. Compare TCEQ Method 1005 chromatograms to one another to determine if the chromatographic profile of the TPH is consistent across the affected property. A change in the distribution of the TPH in the TCEQ Method 1005 chromatographic profile, independent of concentration, may indicate the presence of a different source. For example, in Figure 5 three samples were collected and analyzed using TCEQ Method 1005. As can be seen the chromatographic profiles for samples 1 and 2 are the same, indicating the same source TPH mixture. However, the chromatographic profile for sample 3 is different, indicating a different TPH mixture. Therefore, in the example the affected property includes at least two suspected sources of TPH and therefore PCLs will need to be set for the two different TPH mixtures for application at the respective source area and associated affected area.

Step 3 Compare TCEQ Method 1005 Results to Tier 1 TPH PCLs for the TPH Mixture

If Tier 1 TPH PCLs are available in the TRRP Tier 1 PCL Tables for the specific default composition TPH mixture (for example, Tier 1 PCLs for the default composition for transformer mineral oil), then compare the TPH concentration measurements obtained from TCEQ Method 1005 to the applicable Tier 1 TPH PCLs for the TPH mixture.

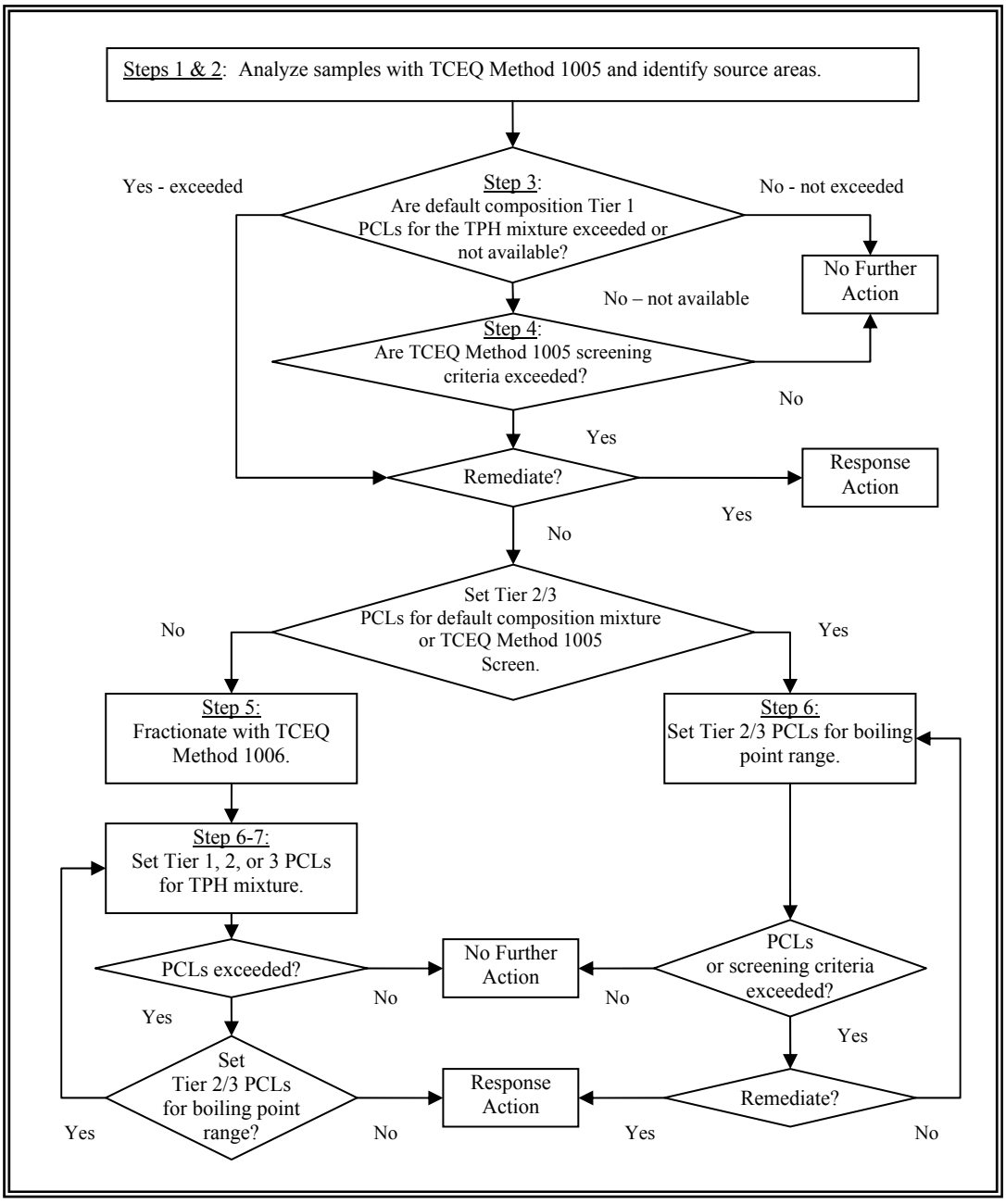

Figure 4. Decision framework for TPH PCL development process.

If the Tier 1 PCLs are not exceeded, then no further action is necessary to address the TPH (Figure 4). If the Tier 1 PCLs are exceeded, then you have several alternatives:

- conduct a response action in accordance with Remedy Standard A or B;
- develop Tier 2 or 3 PCLs for the boiling point ranges and recalculate the PCLs for the TPH mixture using the same default composition; or

- proceed to Step 5; fractionate samples and then proceed to Steps 6 and 7 and establish Tier 1, 2, or 3 PCLs considering the site-specific composition of the TPH mixture(s) at the affected property.

If the relevant Tier 1 PCLs for the specific mixture are unavailable, then proceed to Step 4.

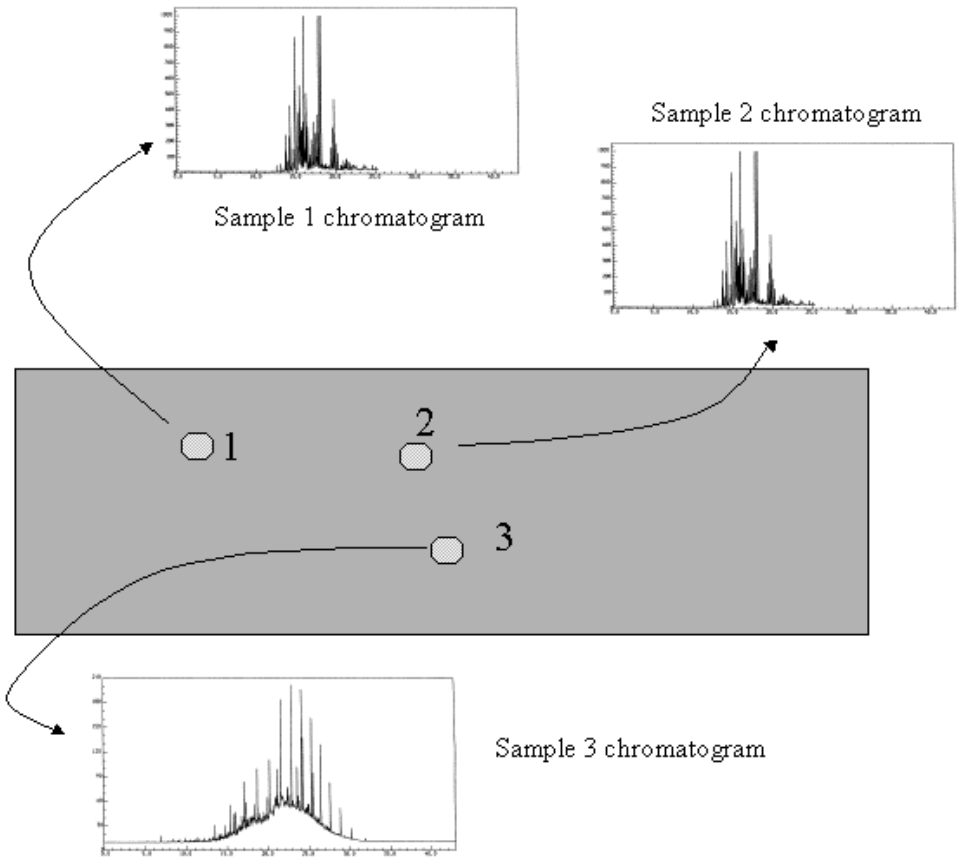

Figure 5. Map view of affected property with sampling locations for TPH samples and corresponding TCEQ Method 1005 chromatographic profiles.

Step 4 TCEQ Method 1005 Results Screening

Compare the concentration measurement for the C_6-C_{12} range obtained from the TCEQ Method 1005 results for each sample to the Tier 1 PCLs for the aromatic >C_8-C_{10} boiling point range appropriate for the exposure pathways applicable to the affected environmental medium as defined in §350.71(c). Then compare the concentration measurement for the C_{12}-C_{28} range, or C_{12}-C_{35} range if applicable, obtained from the TCEQ Method 1005 results for each sample to the Tier 1 PCLs for the aromatic >C_{12}-C_{16} boiling point range appropriate for the exposure pathways applicable to the affected environmental medium as defined in §350.71(c). The development of a PCL for the TPH mixture is only warranted for those

samples where the TCEQ Method 1005 levels exceed the aromatic $>C_8$-C_{10} boiling point range and the aromatic $>C_{12}$-C_{16} boiling point range Tier 1 PCLs.

If either of these Tier 1 boiling point range PCLs are exceeded when compared to TCEQ Method 1005 results, you have several alternatives (Figure 4):

- conduct a response action in accordance with Remedy Standard A or B;
- proceed to Step 6; develop Tier 2 or 3 PCLs for the aromatic $>C_8$-C_{10} and aromatic $>C_{12}$-C_{16} boiling point ranges and re-compare the TCEQ Method 1005 results to those PCLs; or
- proceed to Step 5; fractionate samples and then proceed to Steps 6 and 7 and establish Tier 1, 2, or 3 PCLs considering the site-specific composition of the TPH mixture(s) at the affected property.

Step 5 Fractionate Selected TPH Samples

Select and analyze the sample with the highest TPH concentration from the source area(s) using TCEQ Method 1006 to determine the appropriate PCLs to apply to the source area and its associated affected area. Typically, only a single sample needs to be analyzed from each source area by TCEQ Method 1006. However, for an affected property where different TPH products have been released, multiple TPH samples may need to be analyzed using TCEQ Method 1006 to ensure representative analysis and to establish PCLs for each of the identified TPH source areas. The sample with the highest TPH concentration is needed to allow adequate quality assurance recovery results. The concentration and mass fraction of each boiling point range in each fraction as shown in Figure 3 should be reported. The mass fraction for each boiling point range of the TPH mixture is determined by dividing the concentration of each boiling point range by the total concentration of the TPH mixture.

Step 6 Establish the PCLs for Each Aliphatic and Aromatic Boiling Point Range

Tier 1 PCLs for the aliphatic and aromatic boiling point ranges are available in the Tier 1 PCL Tables for the standard exposure pathways listed in §350.71(c). The PCLs were calculated using the Tier 1 PCL equations provided in Figure: 30 TAC §350.75(b)(1) of the TRRP rule. The surrogate COCs that are to be used to define the toxicity factors for each fraction are presented in Table 1. The COC chemical/physical properties for the boiling point ranges have been extracted from Figure: 30 TAC §350.73(e) of the TRRP rule and are provided in this guidance document as Table 2. For Tiers 2 and 3, site-specific PCLs can be established for

each boiling point range provided the requirements of §350.75 are followed.

Please note that for the >C_{16}-C_{21} and >C_{21}-C_{35} aliphatic boiling point ranges, two different toxicity surrogates are provided. Be certain to use the correct toxicity surrogate. If the TPH is a transformer mineral oil, then use the surrogates for transformer mineral oil releases (for transformer mineral oil releases, >C_{16}-C_{21} and >C_{21}-C_{35} boiling point ranges only) noted in Table 1. Otherwise, use the white mineral oils toxicity surrogate.

Step 7 Establish the PCLs for the TPH Mixture.

To establish the PCL for the complete TPH mixture (i.e., the whole product), for each exposure pathway calculate the inverse weighted average using Equations 1-1 and 1-2. For the soil-to-groundwater PCL (^{GW}Soil), adjustments are needed to account for solubility limitations. Therefore, use Equations 2-1 through 2-5 for this exposure pathway.

Step 8 Select the Critical PCL

For each environmental medium affected by TPH, select the lowest of the PCLs established for the different applicable exposure pathways as the critical PCL.

Step 9 Compare Critical PCL to Representative TPH Concentrations

Compare the established critical PCL for the relevant source area as determined by TCEQ Method 1005 to representative TPH concentrations to identify any exceedances. For all exceedances, you should either pursue a response action under Remedy Standard A or B, or further evaluate TPH PCLs under Tier 2 or 3 if you have not already done so.

Table 1. Hydrocarbon Fractions and Toxicity Factors.

Boiling Point Range	Surrogate for Oral RfD	Surrogate for Inhalation RfC
C_6 Aliphatic	n-hexane	n-hexane[1] commercial hexane[2]
>C_6-C_8 Aliphatic	n-hexane	n-hexane[1] commercial hexane[2]
>C_8-C_{10} Aliphatic	C9-C17 aliphatics	dearomatized white spirits
>C_{10}-C_{12} Aliphatic	C9-C17 aliphatics	dearomatized white spirits
>C_{12}-C_{16} Aliphatic	C9-C17 aliphatics	dearomatized white spirits
>C_{16}-C_{21} Aliphatic	white mineral oils	----
>C_{16}-C_{21} Aliphatic [3]	transformer mineral oil	----
>C_{21-35} Aliphatic[4]	white mineral oil	----

Boiling Point Range	Surrogate for Oral RfD	Surrogate for Inhalation RfC
>C_{21}-C_{35} Aliphatic [3]	transformer mineral oil	----
>C_{7-8} Aromatic	ethylbenzene	ethylbenzene
>C_8-C_{10} Aromatic	multiple aromatic compounds	high flash aromatic naphtha
>C_{10}-C_{12} Aromatic	multiple aromatic compounds	high flash aromatic naphtha
>C_{12}-C_{16} Aromatic	multiple aromatic compounds	multiple aromatic compounds
>C_{16}-C_{21} Aromatic	pyrene	----
>C_{21}-C_{35} [3] Aromatic	pyrene	----

[1]. For mixtures with greater than 53% n-hexane content.

[2]. For mixtures with less than 53% n-hexane content.

[3]. For Transformer Mineral Oil only

[4]. The person may truncate the analysis at C_{28} when there does not appear to be significant mass of >C_{28} based on the gas chromatogram and the product is anticipated to be a lighter hydrocarbon (for example, gasoline, diesel, not transformer mineral oil or used motor oil).

Table 2. COC Properties for TPH Boiling Point Fractions.

Boiling Point Range	Physical State	M.W. (g/mole)	H ' (cm3-H2O/cm3-air)	Log K_{oc}	D_{air} (cm^2/s)	D_{wat} (cm^2/s)	Solubility (mg/l)	Vapor Pressure (mm Hg)
C_6 Aliphatic	liquid	81	3.3E+01	2.9	1.0E-01	1.0E-05	3.6E+01	2.7E+02
>C_6-C_8 Aliphatic	liquid	100	5.0E+01	3.6	1.0E-01	1.0E-05	5.4E+00	4.8E+01
>C_8-C_{10} Aliphatic	liquid	130	8.0E+01	4.5	1.0E-01	1.0E-05	4.3E-01	4.8E+00
>C_{10}-C_{12} Aliphatic	liquid	160	1.2E+02	5.4	1.0E-01	1.0E-05	3.4E-02	4.8E-01
>C_{12}-C_{16} Aliphatic	liquid	200	5.2E+02	6.7	1.0E-01	1.0E-05	7.6E-04	3.6E-02
>C_{16}-C_{35} Aliphatic	liquid	270	4.9E+03	8.8	1.0E-01	1.0E-05	2.5E-06	8.4E-04
>C_7-C_8 Aromatic	liquid	92	2.76E-01	2.15	8.7E-02	8.6E-06	5.3E+02	2.82E+01
>C_8-C_{10} Aromatic	liquid	120	4.8E-01	3.2	1.0E-01	1.0E-05	6.5E+01	4.8E+00
>C_{10}-C_{12} Aromatic	liquid	130	1.4E-01	3.4	1.0E-01	1.0E-05	2.5E+01	4.8E-01
>C_{12}-C_{16} Aromatic	liquid	150	5.3E-02	3.7	1.0E-01	1.0E-05	5.8E+00	3.6E-02
>C_{16}-C_{21} Aromatic	liquid	190	1.3E-02	4.2	1.0E-01	1.0E-05	6.5E-01	8.4E-04
>C_{21}-C_{35} Aromatic	solid	240	6.7E-04	5.1	1.0E-01	1.0E-05	6.6E-03	3.3E-07

M.W. = molecular weight H ' = Henry's Law Constant Log K_{oc} = logarithmic organic carbon partition coefficient
D_{air} = diffusivity in air D_{wat} = diffusivity in water

Equations for calculating PCLs

TPH PCL equations for all exposure pathways other than ^{GW}Soil

$$PCL_{TPH\ Mixture} = \frac{HI}{\sum \frac{MF_i}{PCL_i}} \qquad (1\text{-}1)$$

$$PCL_{TPH\ Mixture} = MIN\left(\frac{PCL_i}{MF_i}\right) \qquad (1\text{-}2)$$

Use (1-1) and (1-2) then set $PCL_{TPH\ Mixture}$ as the lesser of the two.

Explanation of terms for Equations 1-1 and 1-2:

$PCL_{TPH\ Mixture}$ = the generic reference for the PCL for the TPH mixture for the exposure pathway of interest

HI = hazard index; HI must be < 10 (see §350.76(g)(8)).

MF_i = mass fraction of the TPH boiling point range i (Note: varies with TPH mixture, must be calculated for each boiling point range each time assumed TPH mixture composition is changed)

PCL_i = the PCL for TPH boiling point range i from the Tier 1 PCL Tables (or calculated for Tier 2 or 3)

MIN = minimum (PCL_i/MF_i) for all TPH boiling point ranges.

TPH PCL Equations for ^{GW}Soil

Theoretical Maximum $HQ_i = (x_i S_i)/(Ksw_i PCL_i)$ (2-1)

Mole Fraction $x_i = (MF_i / MW_i) / SUM(MF_i / MW_i)$ (2-2)

Theoretical Maximum HI = $SUM(HQ_i + HQ_h + ...)$ (2-3)

If each Theoretical Maximum HQ_i < 1 and the Theoretical Maximum HI is < 10, then the TPH is protective of the underlying groundwater and a ^{GW}Soil PCL does not need to be calculated for the TPH mixture. If the $Soil_{Res}$ concentration is exceeded in the soils, then presence of mobile NAPL is indicated [see TCEQ document *Risk-Based NAPL Management* RG-366/TRRP-32].

Otherwise, use Equation (2-4) OR (2-5) then set $PCL_{TPH\ Mixture}$ as the lesser of the two.

$$PCL_{TPH\ Mixture} = \frac{HI}{\sum \frac{MF_i}{PCL_i}} \quad (2\text{-}4)$$

$$PCL_{TPH\ Mixture} = MIN\left(\frac{PCL_i}{MF_i}\right) \quad (2\text{-}5)$$

Explanation of terms for Equations 2-1 through 2-5:

$PCL_{TPH\ Mixture}$ = the generic reference for the PCL for the TPH mixture for the exposure pathway of interest

HI = hazard index; HI must be < 10 (see §350.76(g)(8)).

HQ_i = hazard quotient of boiling point range i; HQ must be < 1 (see §350.76(g)(8)).

SUM = summation

MF_i = mass fraction of boiling point range i (Note: varies with TPH mixture, must be calculated for each boiling point range each time assumed TPH mixture composition is changed)

MW_i = molecular weight of boiling point range i

PCL_i = the PCL for boiling point range i from the Tier 1 PCL Tables (or calculated for Tier 2 or 3)

MIN = minimum (PCL_i/MF_i) for all boiling point ranges

x_i = mole fraction for boiling point range i; (Note: varies with TPH mixture, must be calculated for each boiling point range each time assumed TPH mixture composition is changed)

S_i = solubility of TPH boiling point range i (mg/l) (see Table 2)

$$Soil_{Res} = \left[\frac{Res.sat \cdot \rho \cdot \theta_T}{\rho_b}\right] \times 1{,}000{,}000 \frac{mg}{kg} = 10{,}000\ \text{mg/kg TPH Mixture}$$

Res.sat = (10,000 mg/kg x ρ_b)/(1,000,000 mg/kg x ρ x θ_T), Tier 1 default: 0.045

ρ = density of the non-aqueous phase liquid (g/cm^3) Tier 1 default: 1

θ_T = total soil porosity (cm^3-pore space/cm^3-soil) = 1- (ρ_b/ρ_s) Tier 1 default: 0.37

ρ_b = soil bulk density (g/cm^3), Tier 1 default: 1.67

ρ_s = particle density (g/cm^3), Tier 1 default: 2.65

$$K_{sw}\left[\frac{(mg/L\text{ - }H_2O)}{(mg/kg\text{ - soil})}\right] = \frac{\rho_b}{\theta_{ws} + K_d\rho_b + H'\theta_{as}}$$

K_{sw} = Soil-leachate partition factor for COC (Note: varies with affected property parameter assumptions and not TPH mixture, therefore, may vary only under Tier 2 or 3); K_d = soil-water partition coefficient (cm^3-water/g-soil) (see Table 2); $K_d = K_{oc}$ x foc

θ_{ws} = Volumetric water content of vadose zone soils (cm^3-water/cm^3-soil), Tier 1 default: 0.16

K_{oc} = soil organic carbon-water partition coefficient (cm^3-water/g-carbon) (see Table 2)

foc = fraction of organic carbon in soil (g-carbon/g-soil), Tier 1 default: 0.002

H′ = dimensionless Henry's Law Constant (see Table 2)

θ_{as} = volumetric air content of vadose zone soils (cm^3-air/cm^3-soil), Tier 1 default: 0.21.

Case Study For Setting TPH PCLs for a TPH Mixture

For this case study, it is assumed that field sampling has been conducted (Step 1), the source area has been identified (Step 2), the TCEQ Method 1005 analytical results have been compared to the default composition Tier 1 TPH PCLs where available (Step 3), the TCEQ Method 1005 screening level PCLs have been exceeded (Step 4), and the TPH mixture has been fractionated by TCEQ Method 1006 (Step 5). The provided Tier 1 PCLs for each boiling point range are being used to determine the site-specific TPH mixture PCL (Step 6). The case study begins with examples on how to establish the PCLs for the site-specific mixture (Step 7).

The analytical results (presented in Table 3) were obtained from the fractionation of the TPH mixture using TCEQ Method 1006.

Table 3. Mass Fraction for Each Aliphatic and Aromatic Boiling Point Range (determined from Step 5).

Boiling Point Range	Mass Fraction (MF_i)	Concentration (C_i) (mg/kg)
C_6 Aliphatic	0.00E+00	0
>C_6-C_8 Aliphatic	6.40E-04	0.32
>C_8-C_{10} Aliphatic	3.04E-03	1.52
>C_{10}-C_{12} Aliphatic	7.72E-03	3.86
>C_{12}-C_{16} Aliphatic	1.81E-01	90.62
>C_{16}-C_{21} Aliphatic	5.96E-01	297.79
>C_{21}-C_{35} Aliphatic	2.09E-01	104.74
>C_7-C_8 Aromatic	0.00E+00	0
>C_8-C_{10} Aromatic	0.00E+00	0
>C_{10}-C_{12} Aromatic	0.00E+00	0
>C_{12}-C_{16} Aromatic	8.00E-04	0.4
>C_{16}-C_{21} Aromatic	1.30E-03	0.65
>C_{21}-C_{35} Aromatic	2.20E-04	0.11
Sum Aliphatic Fraction	**0.998**	**498.85**
Sum Aromatic Fraction	**0.002**	**1.16**
Total TPH	**1.00**	**500.01**

Step 5. Determine the mass fraction (MF_i) of each TPH aliphatic and aromatic boiling point range.

The mass fraction (MF_i) of each TPH aliphatic and aromatic boiling point range must first be calculated using the following equation:

$$MF_i = \frac{C_i}{\text{Total TPH}}$$

For example, calculate MF_i for the $>C_{21}$-C_{35} aliphatic boiling point range using the results from Table 3, above:

$$MF_i = \frac{C_i}{\text{Total TPH}} = \frac{104.74\ \text{mg/kg}}{500.01\ \text{mg/kg}} = 2.09\text{E}-01$$

Step 6. Determine the Tier 1 PCLs (PCL_i) for each exposure pathway for each aliphatic and aromatic boiling point range

In this example, the human health PCL ($^{Tot}Soil_{Comb}$) and soil-to-groundwater PCL ($^{GW}Soil$) are calculated for surface soil, based on residential land uses and 0.5 acre source area assumptions. The Tier 1 PCLs for each boiling point range for these exposure pathways are presented in Tables 4 and 5, respectively.

PCLs have already been calculated for the two exposure pathways being considered for each aliphatic and aromatic boiling point range for Tier 1. Those PCLs were used here. The Tier 1 PCLs were calculated using the PCL equations as presented in Figure: 30 TAC §350.75(b)(1), the toxicity information presented in Table 1, and the COC chemical/physical properties presented in Table 2 of this document. To establish Tier 2 or 3 PCLs for the individual boiling point fractions, site-specific information would be used in accordance with §350.75(c) and (d) in lieu of Tier 1 default assumptions.

Step 7 Determine the PCL for the TPH mixture ($PCL_{TPH\ Mixture}$).

Use Equations (1-1) through (2-5) as appropriate for the particular exposure pathway to determine the $PCL_{TPH\ mixture}$.

The Surface Soil Human Health Exposure Pathway ($^{Tot}Soil_{Comb}$)

1. Calculate MF_i, MF_i/PCL_i, PCL_i/MF_i

The mass fraction (MF_i), and the ratios of MF_i/PCL_i and PCL_i/MF_i, must first be calculated. The results for this example are presented in Table 4.

2. Calculate $^{Tot}Soil_{Comb}$ using Equations (1-1) and (1-2) and set the PCL as the lesser of the two.

A. From Equation (1-1) and Table 4:

$$PCL_{TPHMixture}\ ^{Tot}Soil_{Comb} = \frac{HI}{\sum \frac{MF_i}{PCL_i}} = \frac{10}{7.86\text{E}-05\ \text{kg/mg}} = 1.27\text{E}+05\ \text{mg/kg}$$

B. From Equation (1-2) and Table 4:

$$PCL_{TPHMixture}{}^{Tot}Soil_{Comb} = MIN\left(\frac{PCL_i}{MF_i}\right) = 1.54E+04 \text{ mg/kg}$$

The minimum of the two PCLs is 1.54E+04 mg/kg ($^{Tot}Soil_{Comb}$ for the TPH mixture).

The soil-to-groundwater ($^{GW}Soil$) pathway

To determine the soil-to-groundwater PCL ($^{GW}Soil$) for the TPH mixture, the same criteria as above must be met. That is, HQ_i must be ≤1 and HI must be ≤10. However, the effective solubility of the TPH mixture components should be considered when determining $^{GW}Soil$. Therefore, Equations (2-1) through (2-5) are used.

The potential for the TPH mixture to generate unprotective leachate is limited by the solubility of the mixture. If $HQ_i \leq 1$ for each boiling point range and HI ≤10, then the leachate is protective for the underlying groundwater because of solubility limits and the $^{GW}Soil$ PCL does not need to be calculated for the TPH mixture. The reason the $^{GW}Soil$ PCL does not need to be calculated is that the TPH mixture cannot dissolve enough TPH into the groundwater to exceed the groundwater PCLs, regardless of the concentrations of that TPH mixture in the soils. However, irregardless of whether or not the development of the $^{GW}Soil$ PCL is warranted in consideration of solubility limits, if the TPH mixture concentration in soils at the affected property exceeds the Tier 1 $Soil_{Res}$ value of 10,000 mg/kg, then the presence of mobile non-aqueous phase liquids (NAPLs) is indicated [see RG-366/TRRP-32 *Risk-Based NAPL Management*]. All calculation results for this $^{GW}Soil$ example are presented in Table 5.

Table 4. Calculation results for the TPH mixture Case Example for $^{Tot}Soil_{Comb}$ Residential Land Use (0.5 acre).

Boiling Point Range	MF_i	$^{Tot}Soil_{Comb}$ PCL_i (mg/kg)	MF_i/PCL_i $(mg/kg)^{-1}$	PCL_i/MF_i (mg/kg)	HQ_i
C_6 Aliphatic	-	1.90E+03	-	-	-
> C_6-C_8 Aliphatic	6.40E-04	1.90E+03	3.39E-07	2.95E+06	5.23E-03
> C_8-C_{10} Aliphatic	3.04E-03	2.20E+03	1.38E-06	7.24E+05	2.13E-02
> C_{10}-C_{12} Aliphatic	7.72E-03	2.10E+03	3.68E-06	2.72E+05	5.68E-02
> C_{12}-C_{16} Aliphatic	1.81E-01	2.80E+03	6.47E-05	1.54E+04	1.00E+00
> C_{16}-C_{21} Aliphatic	5.96E-01	1.30E+05	-	-	-
> C_{21}-C_{35} Aliphatic*	2.09E-01	1.10E+05	7.32E-06	1.37E+05	2.15E-05
> C_7-C_8 Aromatic	-	4.80E+03	-	-	-
> C_8-C_{10} Aromatic	-	1.60E+03	-	-	-

Boiling Point Range	MF_i	$^{Tot}Soil_{Comb}$ PCL_i (mg/kg)	MF_i/PCL_i $(mg/kg)^{-1}$	PCL_i/MF_i (mg/kg)	HQ_i
> C_{10}-C_{12} Aromatic	-	1.90E+03	-	-	-
> C_{12}-C_{16} Aromatic	8.00E-04	2.30E+03	3.48E-07	2.88E+06	5.37E-03
> C_{16}-C_{21} Aromatic	1.30E-03	1.90E+03	6.84E-07	1.46E+06	1.06E-02
> C_{21}-C_{35} Aromatic	2.20E-04	1.90E+03	1.16E-07	8.64E+06	1.79E-03
		SUM =	**7.86E-05**	**1.54E+04**	
				HI =	**1.10E+00**

* > C_{16}-C_{21} Aliphatic and C_{21}-C_{35} Aliphatic are lumped for convenience because the toxicity surrogate is the same for both boiling point ranges for the TPH mixture.

1. Determine the theoretical maximum HQ_i and HI for the TPH mixture:

A. Calculate the mole fraction (x_i) for each boiling point range using Equation (2-2).

$$X_i > C_{16} - C_{35}\ \text{aliphatic} = \frac{\frac{MF_i}{MW_i}}{\Sigma\left(\frac{MF_i}{MW_i}\right)} = \frac{\frac{5.96E-01 + 2.09E-01}{270\ g/mol}}{3.98E-03\ (g/mol)} = 7.50E-01$$

B. Calculate the hazard quotient (HQ) for each boiling point range using Equation (2-1).

$$HQ_i > C_{16} - C_{35}\ \text{aliphatic} = \frac{X_i S}{K_{swi} PCL_i} = \frac{7.50E-01 \text{ x } 2.5E-06\ mg/l}{7.92E-07\ (mg/l\text{ - water/ }mg/kg\text{ - soil}) \text{ x } 1.10E+05\ mg/kg} = 2.15E-05$$

C. Calculate the hazard index (HI) using Equation (2-3).

$$HI = \sum(HQ_1 + HQ_2 + HQ_3 .....) = 1.10E+00$$

As shown in Table 5, $HQ_i \leq 1$ for each boiling point fraction and HI ≤ 10, therefore the TPH mixture does not pose a threat to the underlying groundwater, and therefore ^{GW}Soil does not need to be calculated. However, in order to to provide a complete set of example calculations, ^{GW}Soil PCLs are calculated using Equations (2-4) and (2-5) even though it is not warranted in this particular case study.

2. Determine ^{GW}Soil as the lesser of PCLs calculated from Equations (2-4) and (2-5).

Solving for Equation (2-4):

$$PCL_{TPHMixture}{}^{GW}Soil = \frac{HI}{\sum \frac{MF_i}{PCL_i}} = \frac{10}{1.07E-05\ (kg/mg)} = 9.35E+05\ mg/kg$$

Solving for Equation (2-5):

$$PCL_{TPH\ Mixture}{}^{GW}Soil = MIN\left(\frac{PCL_i}{MF_i}\right) = 2.50E+05\ mg/kg$$

Table 5. Calculation results for ^{GW}Soil for the TPH mixture Case Example.

Boiling Point Range	MF_i	MF_i/ MW_i	^{GW}Soil PCL_i (mg/kg)	xi	MF_i/ PCL_i $(mg/kg)^{-1}$	PCL_i/ MF_i (mg/kg)	HQ_i
C_6 Aliphatic	-	-	1.70E+02	-	-	-	-
> C_6-C_8 Aliphatic	6.40E-04	6.40E-06	4.20E+02	1.61E-03	1.52E-06	6.57E+05	2.96E-04
> C_8-C_{10} Aliphatic	3.04E-03	2.34E-05	3.60E+03	5.88E-03	8.47E-07	1.18E+06	5.17E-05
> C_{10}-C_{12} Aliphatic	7.72E-03	4.82E-05	2.50E+04	1.21E-02	3.05E-07	3.28E+06	8.43E-06
> C_{12}-C_{16} Aliphatic	1.81E-01	9.06E-04	4.90E+05	2.28E-01	3.67E-07	2.72E+06	3.54E-06
> C_{16}-C_{21} Aliphatic	5.96E-01	-	1.00E+06	-	-	-	-
> C_{21}-C_{35} Aliphatic	2.09E-01	2.98E-03	1.00E+06	7.49 E-01	8.05E-07	1.24E+06	1.94E-06
> C_7-C_8 Aromatic	-	-	2.00E+01	-	-	-	-
> C_8-C_{10} Aromatic	-	-	6.50E+01	-	-	-	-
> C_{10}-C_{12} Aromatic	-	-	1.00E+02	-	-	-	-
> C_{12}-C_{16} Aromatic	8.00E-04	5.33E-06	2.00E+02	1.34E-03	4.00E-06	2.50E+05	3.94E-04
> C_{16}-C_{21} Aromatic	1.30E-03	6.84E-06	4.70E+02	1.72E-03	2.77E-06	3.62E+05	7.56E-05
> C_{21}-C_{35} Aromatic	2.20E-04	9.17E-07	3.70E+03	2.30E-04	5.95E-08	1.68E+07	1.04E-07
	SUM=	**3.98E-03**			**MIN=**	**2.50E+05**	
				SUM =	**1.07E-05**	**HI =**	**8.31E-04**

Step 8. Choose the Critical Surface Soil PCL for this TPH mixture example.

To determine the critical PCL, the PCLs for each of the exposure pathways applicable to the affected environmental medium must be compared. Table 6 below presents all the residential PCLs prescribed in the Tier 1 PCL table that would apply for surface and subsurface soils.

The critical PCL is the lowest of the pathway specific PCLs. For this TPH mixture, the critical surface soil PCL is 1.54E+04 mg/kg (the lower of $^{Tot}Soil_{Comb}$ and ^{GW}Soil), assuming mobile NAPL is not present in soils and $Soil_{Res}$ is not limiting.

Table 6. Critical PCLs for TPH mixture for Residential Soil Exposures.

Exposure Pathway:	$^{Tot}Soil_{Comb}$ (mg/kg)	$^{Air}Soil_{Inh\text{-}V}$ (mg/kg)	$^{GW}Soil$* (mg/kg)	
PCL:	1.54E+04[1]	2.65E+04[2]	2.50E+05[3]	
		Critical PCL for Surface Soils:		**1.54E+04**
		Critical PCL for Subsurface Soils:		**2.65E+04**

[1] applies to surface soil only

[2] applies to subsurface soil only

[3] applies to surface and subsurface soils

* the ^{GW}Soil PCL was not actually required for this particular example

Frequently Asked Questions

Question 1: When do I consider TPH in my assessment?

Answer 1: You make the decision to include TPH in an assessment in conjunction with the applicable program area. In addition, the TCEQ guidance document *Selecting Target COCs* (RG-366/TRRP-10) provides further information on selecting chemicals of concern for analysis.

Question 2: Are TCEQ Methods 1005 and 1006 the only methods that can be used to determine concentrations of TPH in environmental media?

Answer 2: Other methods can be used. However, to use an alternate method, a proposal to use an alternate method that includes the data needed to validate the alternate method against TCEQ Method 1005 and 1006 as the reference methods must be submitted to the agency. Once the use of an alternate method has been approved, additional proposals to use that method will not be needed. The TCEQ will update a list of additional methods and will have the list available on the TRRP Web page. See Question 5 below for a related matter.

Question 3: When do I compare site data directly to boiling point range PCLs listed in the Tier 1 PCL tables versus calculating a PCL for the entire TPH mixture?

Answer 3: The only time the PCLs included in the Tier 1 PCL tables for the boiling point ranges (e.g., $>C_8$-C_{10} aromatic) should be directly compared to TCEQ Method 1005 results is when conducting the TCEQ Method 1005 screen as explained earlier in Step 4.

Question 4: Is there double counting of compounds when there is COC-specific analytical data (for example, benzene concentrations in soil) and assessment of TPH is required?

Answer 4: The TPH approach described in this document only addresses the noncarcinogenic effects of each fraction. The toxicity endpoint of concern for benzene and the carcinogenic polycyclic aromatic hydrocarbons is different than that of TPH as a mixture. For benzene, TCEQ Method 1006 does not characterize the C_6 aromatic fraction, which is the fraction of interest for benzene. Double counting might be a concern when using historical data. For example, some petroleum hydrocarbons are detected in both the Method 8015 gasoline range organics and diesel range organics analyses. Concentrations of individual VOCs or SVOCs

should be characterized by methods such as EPA Methods 8260 or 8270, respectively.

Question 5: Is it possible to use historical data yielded from other (non-TCEQ Method 1005 or 1006) analytical methods?

Answer 5: The use of historical data collected prior to the implementation of the TRRP rule will be evaluated on a case-by-case basis, which will consider the assumptions being made in interpreting the data to ensure that those data meet project objectives. The historical data should allow for the qualitative evaluation of the distribution of hydrocarbons within the mixture and quantitation of the mixture between the C_6-C_{28}, or when applicable, C_6-C_{35}boiling point ranges. The data should provide quantitation of the petroleum hydrocarbons within each of the boiling point ranges for each fraction listed in Table 1.

Question 6: How do I develop Tier 2 PCLs?

Answer 6: To calculate Tier 2 PCLs for the TPH mixture, calculate Tier 2 PCLs for each boiling point range present in the TPH mixture using site-specific information in the Tier 2 PCL equations in accordance with §350.75(c). Then use Equations (1-1) through (2-5) in this document to develop Tier 2 TPH PCLs for the TPH mixture using the Tier 2 PCLs developed for each boiling point range.

Product Composition and Weathering

Once a petroleum hydrocarbon product (e.g., gasoline, diesel, etc.) has been released into the environment, the chemical composition (i.e., the petroleum hydrocarbon makeup) can change over time. This change could be attributed to the commingling of different petroleum hydrocarbon mixtures released into the same area resulting in a new mixed composition of TPH, or environmental weathering of the petroleum hydrocarbons. For example, a release of gasoline onto the soil in the month of July will undergo significant changes within the first five hours after the release due to the volatility of the petroleum hydrocarbons in the gasoline. The extent and rate of change in the released mixture depends on the type of petroleum hydrocarbons that make up the TPH, the number of mixtures that contributed to the TPH source area (source area as defined by 30 TAC §350.4(a)(84)), prevailing weather conditions, fate and transport aspects such as the rate of biodegradation and the potential of the TPH to undergo partitioning as it interacts with environmental media into which it is released.

You can use chemical analysis of a product by gas chromatography to determine the specific mixture of hydrocarbons in that product so that a PCL can be developed. The chemical analysis is based on a comparison of the boiling point ranges for the petroleum hydrocarbons in the product relative to the boiling points for the normal alkane hydrocarbon series. This series extends from normal methane (n-C_1) and to beyond normal hexatriacontane (n-C_{36}). For example, the TPH in crude oil is composed of petroleum hydrocarbons between the boiling point ranges from n-C_1 to beyond n-C_{34}. Refined products from crude oil include: (1) gasolines which characteristically have TPH composed of hydrocarbons between the boiling point ranges of normal hexane (n-C_6) and normal dodecane (n-C_{12}); (2) diesel fuels with TPH characteristically composed of hydrocarbons found between the boiling point ranges of normal octane (n-C_8) and normal heneicosane (n-C_{21}); and (3) motor oils having a characteristic TPH composition from normal octadecane (n-C_{18}) to beyond n-C_{36}.