Section 2 Introduction: Printed from Interstate Technology & Regulatory Council (ITRC). 2018. TPH Risk Evaluation at Petroleum-Contaminated Sites. THPRisk-1. Washington, D.C.: Interstate Technology & Regulatory Council, TPH Risk Evaluation Team. https://tphrisk-1.itrcweb.org

2 Introduction

The term “TPH” is often used to refer to the broad range of chemicals comprising petroleum hydrocarbons (see Definition of TPH Fact Sheet). The approaches to assess cumulative risk posed by the multitude of petroleum-related compounds (or mixtures) typically included under the term “TPH” have yet to be widely accepted and employed. Some state programs do not require corrective action based on bulk TPH measurements and use only indicator compounds in their risk assessments while others require a combination of indicator and bulk TPH measurements for decision making.

Risk characterization based on TPH concentration measurements in different environmental media may be used to inform corrective actions or risk management decisions at petroleum release sites. This applies to assessment of potential human health risks as well as ecological risks, which can be challenging because chemical compositions of petroleum hydrocarbon mixtures are complex and subject to change over time due to fate and transport processes (e.g., weathering processes such as biodegradation, dissolution, and volatilization).

TPH screening levels, toxicity value surrogates, and cleanup levels (if any) are inconsistently used across the states. Some states consider the detection of TPH using a variety of methods as evidence of a petroleum release, some use TPH screening level(s), and others do not use TPH analyses at all. The inconsistent approaches stem in part from the uncertain toxicology of TPH ranges, which is due in part to highly variable composition. When published lookup table values are available, they may be misused (e.g., lookup table values used as cleanup levels in cases where it may be more appropriate to consider these values for decision making regarding additional site characterization).

Consistent methodologies and streamlined approaches for establishing risk-based cleanup of TPH-contaminated media are necessary and will assist in the development of evidence-based, technically defensible approaches for risk-based assessments and remediation decision making at petroleum release sites.

▼*Read more*

TPH is defined as the measurable amount of petroleum-based hydrocarbon in an environmental media, and it is dependent on analysis of the medium in which it is found TPHCWG 1997b. TPH is a gross quantification of the petroleum mixture without identification of individual constituents and can be measured using one of several analytical methods. Depending on the analytical method used, TPH measurements may not always represent petroleum hydrocarbons but rather a broader total organics measurement. The measured TPH value represents a mixture; however, the analytical method may not limit the quantification solely to hydrocarbons (i.e., compounds containing only hydrogen and carbon). The resulting concentration can include nonhydrocarbons, such as naturally occurring organic matter, chemicals, and metabolites (i.e., degradation byproducts). Understanding the physical and chemical properties of petroleum hydrocarbons as well their behavior in the environment is essential in the development of risk-based approaches.

As illustrated in the gas chromatograms presented in Figure 2-1, the distributions of hydrocarbons are quite different for different products. A more in-depth discussion on petroleum chemistry is provided in TPH Fundamentals.

Figure 2-1. Example analytical chromatograms for petroleum mixtures and petroleum products.
(Source: Texas Commission on Environmental Quality,2010.)

There are refined analytical methods for TPH that provide an improved approach for identifying and characterizing the extent of petroleum releases. However, the indicator compounds (e.g., BTEXN) can be missed due to high detection limits in highly contaminated media. The absence of BTEXN is often misinterpreted as the absence of contamination and lack of any risk.

Some regulatory programs link the bulk TPH concentrations to the presence of light nonaqueous phase liquids (LNAPL). LNAPL is present when TPH concentrations in soil are sufficient for LNAPL to occur in the pore space or when dissolved-phase concentrations exceed solubility limits considering the petroleum hydrocarbon mixture. Discussion of risks associated with

LNAPL is not included in this document. Details regarding risk-based decision making at LNAPL sites are available in ITRC LNAPL-3 2018.

2.1 Issues Unique to TPH

Issues unique to TPH are attributed to:

- differing composition of complex mixtures
- different analytical methods (critical because TPH values are method-dependent) and interpretation
- degradation mechanisms and understanding
- varying regulatory approaches
- the presence of petroleum metabolites

As noted, common tiered approaches to risk evaluation, either through the comparison with published screening levels or the development of site-specific screening levels, need to be nuanced and better understood in a TPH risk evaluation. For example, it is common to compare a TPH analytical result to published screening levels; however, the composition of constituents that makes up TPH will vary based on the source of the release and other considerations (see Biodegradation) and may differ from the assumed composition that was used to develop the published screening level. Other approaches (e.g., Tier 3) to quantifying risk may be appropriate for some release sites.

As illustrated in Figure 2-2, petroleum products are complex mixtures. Note that this figure is a conceptual figure to illustrate the different classes of contaminants that may be detected at petroleum release sites and the makeup for specific sites will be different from what is shown in this figure. Contamination at petroleum release sites is likely to consist of a mixture of the original petroleum hydrocarbon compounds (i.e., compounds consisting primarily of carbon and hydrogen atoms, although petroleum mixtures may also contain some other compounds that include nitrogen, sulfur, or oxygen atoms), petroleum-related degradation products (e.g., “metabolites” associated with biologic breakdown of parent compounds), fuel additives (e.g., oxygenates and lead scavengers), and to a limited extent, fuel impurities.

For the purposes of this document, TPH is defined by the aliphatic and aromatic hydrocarbon carbon range fractions covering the applicable carbon range based on the known or assumed original hydrocarbon mixture (or the weathered hydrocarbon mixture thereof), or the hydrocarbon fractions partitioned to water or air. Additionally, TPH analytical results do not distinguish between natural (e.g., crude oil seeps) and anthropogenic sources. A complicating factor for the assessment of risk posed by TPH- and petroleum-related degradation products (which by definition are not “hydrocarbons”) that might be reported under many analytical methods, is the potential presence of similar compounds in soil or water that are unrelated to the petroleum release. Because different combinations of petroleum hydrocarbons can contribute to TPH at different sites, the human health and ecological effects associated with TPH can be dissimilar at different petroleum release sites, even if the TPH concentration is the same.

Figure 2-2. Conceptual illustration of contaminants at petroleum release sites.

▼*Read more*

The thousands of compounds associated with TPH- and petroleum-related degradation compounds span a wide range of chemical, physical, and toxicological properties. Because of this complexity, a variety of laboratory analytical methods to quantify TPH concentrations in different environmental media have been used historically and/or are available today (see Conceptual Site Models), and no single method encompasses all components and breakdown products of TPH. Bulk analysis involves reporting petroleum hydrocarbon concentrations in aggregate, as a single, total number (e.g., TPH, gasoline range TPH, total volatile hydrocarbons, etc.). These data may also be reported by groups with similar volatility (i.e., equivalent carbon number). Individual compounds known to be included in TPH may be measured and used to represent TPH as indicator compounds. Fractionation methods separate petroleum compounds into two broad classes, aliphatics and aromatics, based on distinct chemical behavior. Note, however, that not all petroleum compounds or metabolites may be quantified in a particular TPH laboratory analysis (see Definition of TPH Fact Sheet and TPH Analytical Methods Fact Sheet).

Different methods can produce different results for the same sample Zemo 2016. In addition, petroleum-related degradation

compounds (which are not strictly considered to be hydrocarbons, because these compounds contain oxygen) will often be reported in combination with parent petroleum compounds in TPH test methods that do not include removal of polar compounds, a step referred to as silica gel cleanup. This step may or may not be acceptable, depending on the data quality objectives of the investigation and state regulatory requirements. Some regulatory agencies assume for initial screening purposes that petroleum-related degradation products have a similar toxicity as the parent compounds and require data for samples both with and without degradation compounds removed as part of a risk assessment CASWB-SFBR 2016a, 2016b; HIDOH 2017; WADOE 2016a, 2016b (see Human Health Risk Assessment or Ecological Risk Assessment).

Because TPH data are dependent on the analytical method used for a particular sample, use of historical TPH measurements for risk characterization may require special consideration and interpretation (see Case Studies). Additionally, toxicity studies for TPH mixtures have not gone through the same level of peer review as the indicator compounds that are considered at petroleum release sites, so this will increase the uncertainty of the human health and ecological risk characterization estimates.

The consideration of TPH and other petroleum-related compounds (e.g., metabolites) that are not addressed individually in a risk assessment is important. Evaluation of the composition of petroleum products, including gasoline, crude oil, jet fuels, kerosene, diesel, home heating oils, and lubricating oils, identified up to 250 constituents with available physical properties TPHCWG 1998b. Hydrocarbons can degrade in the subsurface where microbes and sufficient moisture content are present. Degradation of parent compounds adds to the complexity of an ever-changing mixture of compounds. Obtaining analytical data for each of these individual constituents and/or degradation components is unrealistic and cost prohibitive. In addition, the development of theoretical data requires a series of broad assumptions. Furthermore, the toxicity data and fate and transport modeling parameters required for the assessment of human and ecological health risk are currently not available for most of these individual compounds.

The most common approaches used to address human health and ecological risks posed by these compounds include

- Evaluation of whole products
- Reliance on a short list of targeted indicator compounds
- Use of carbon range fractions

(See Regulatory Framework, Human Health Risk, and Ecological Risk Assessment for more information).

Additionally, ecological risks may include consideration of other compositional aspects of the hydrocarbon mixture (e.g., low molecular weight versus high molecular weight fractions). Some combination of these approaches may be used for TPH risk characterization. Ecological risks may also be evaluated using site-specific toxicity testing approaches using the above-listed analyte definitions or by using operationally defined fractions, such as water-soluble fractions (WSFs) or water-accommodated fractions (WAFs).

Comparison of whole product TPH concentration data (e.g., TPH as gasoline or TPH as diesel) to risk-based screening levels based on assumed carbon range compositions of fuels is used by some states to directly assess risk to human health and the environment ITRC 2015; HIDOH 2017. Use of whole product data may be appropriate for petroleum releases from known sources (for example, tank failures onto secondary containment, fuel releases from pipelines and trucks, etc.). Alternatively, the toxicities of well-studied indicator compounds such as BTEXN represent the toxicity of the petroleum mixture as a whole and have been used to develop screening levels for TPH.

Under the second approach, data for individually targeted indicator compounds are used to evaluate the risk posed by complex mixtures, even though they might make up a small fraction of the total compounds present. If calculation of risk or comparison to screening levels specific to these chemicals suggested minimal risks, then no further action was required. This led in some cases to a premature and potentially erroneous conclusion that the risk posed by the “TPH” component of the contamination and associated degradation products will be minimal if the risk posed by individual indicator compounds falls within acceptable levels. Additional details on these items are presented in the discussions on toxicity assessment, ecological risk assessment, and risk calculators.

This document recommends a combined individual chemical approach, and carbon range approach and presents guidelines on how to carry out this combination.

The fraction approach involves resolving petroleum constituents into fractions based on chemical properties and then

assigning representative toxicity criteria to each fraction. This allows screening levels to be developed or risk directly calculated for individual carbon ranges in the same manner as is done for individual compounds. Several regulatory agencies (see States Survey) have published guidance that employs fractions along with indicator compounds for assessment of potential contaminated sites MADEP 2002b; WADOE 2016a; CASWB-SFBR 2016a; HIDOH 2017; TCEQ 2017a, 2017b.

The Conceptual Site Models and Investigative Strategies section compares the different methods currently approved for use by the state regulatory agencies. The TPH Criteria Working Group (TPHCWG) guidance advocated the use of benzene and carcinogenic polycyclic aromatic hydrocarbons (PAHs) as indicator compounds to evaluate human health cancer risk at such sites and assessment of 13 TPH fractions for evaluation of noncancer hazards TPHCWG 1997a. Evaluation of ecological risk would not involve consideration of cancer end points.

Quantification of TPH in contaminated media is based on the analytical method that is used. Selection of analytical methods for TPH characterization is important because different analytical methods may yield entirely different results for a given sample. Common analytical techniques include gas chromatography (GC), infrared spectrometry, gravimetry, immunoassay, and liquid chromatography. Similarities and differences between these methods are discussed in Conceptual Site Models and Investigative Strategies. Most common analytical methods include the following steps, and each influences the identification of TPH constituents and compositional data reporting:

1) Collection and preservation for applicable media (soil, water, vapor, etc.)

2) Extraction techniques (methylene chloride, etc.)

3) Adjustment for compound interferences

4) Adjustment for concentration dilutions

5) Quantification of analytes

The same concentration of TPH in different areas of a site might include dissimilar fractions, which, in turn, may represent different risks to human or ecological health and the environment. For example, samples from two different sites may have similar TPH concentrations; however, the composition and weathering of the petroleum hydrocarbons may be significantly different (Figure 2-3).

Figure 2-3. TPH composition changes.

The risk at a specific site will change with time due to weathering/degradation. Some states recommend the collection of carbon range data as part of the site investigation and assessment of risk MADEP 2002a; ORDEQ 2011; WADOE 2016a; TCEQ 2017a, 2017b. In practice, some combination of both approaches is often used, with site-specific carbon range data being used to develop more site-specific screening levels and bulk TPH data being used to identify areas of potential concern and develop remediation plans (see States Survey). For example, bulk analyses may be used for scoping mass removal/reduction cleanups, but fractionated data are more appropriate for risk evaluations. However, bulk TPH data may be acceptable for cases of fresh spills of known origins. Examples of both approaches are presented in the Case Studies.

2.2 Applicability of Guidance

This section describes the types of products and sites that are addressed in this guidance. Additionally, human health and ecological risk assessment considerations to be covered are described.

2.2.1 Types of Petroleum Products

This guidance is intended to be applicable for releases of crude oil or refined petroleum products. Refineries produce different suites of petroleum products, with the largest percentage of products being various grades of fuel oil and gasoline. Heavier (less volatile) fractions can also be used to produce asphalt, tar, paraffin wax, and lubricating and other heavy oils. Petroleum products can also be used to describe Stoddard solvent, aviation gas, paint thinner, mineral spirits, bunker oil, jet fuel, kerosene, diesel, motor oil, heating oil, residual fuels, and many refinery intermediates. The various TPH analyses are

capable of identifying and quantifying the presence of these products in contaminated media. A more detailed description of petroleum products and potential sources is provided in ITRC 2014 (ITRC PVI Guidance).

2.2.2 Types of Sites

TPH contamination may be detected at sites that store, handle, or use petroleum products at both marine and land releases (see Case Studies). In some instances, neighboring properties impacted by petroleum releases (e.g., downgradient of initial release locations) may have different land uses, such as residential, commercial, or institutional properties, than the release locations. The guidance is applicable for a variety of petroleum sites ranging from smaller sites, such as gas stations with underground or aboveground storage tanks, residential heating oil tanks, or tanker truck spills, to larger petroleum industrial sites, such as bulk storage and distribution terminals, refineries, pipelines, or manufactured gas plants. Additionally, TPH impacts may be identified during property redevelopment, and TPH contamination is often found at historical and active industrial sites. Changes in land use (e.g., redevelopment of commercial or industrial properties for residential land use) also should be considered during site characterization. Lastly, TPH impacts could be encountered from tanker truck or barge fuel releases onto urban and rural areas or through discharges from pipelines that carry crude oil and refined products.

2.3 Background of Current Approaches

Historically, remediation of TPH in soil or groundwater was based on generic screening levels (e.g., 100 mg/kg TPH in soil) or aesthetic considerations (visible presence of oil or odor). In the 1990s, frameworks were developed to characterize TPH risks based on a fraction approach (MADEP 1994; TPHCWG 1998a; WADOE 1997) (see History of TPH Regulation). The fraction approach was used to account for the different chemical, fate and transport, physical, and toxicological properties of different classes of hydrocarbons. Key components of this fraction approach include:

▼*Read more*

- Analytical characterization—fractions based on distinguishing aromatic and aliphatic components as well as molecular weight
- Fate and transport parameters—representative chemical and physical properties were selected for different hydrocarbon fractions based on surrogate chemicals for each fraction
- Toxicity characterization—representative toxicity factors were selected for different hydrocarbon fractions based on surrogate chemicals for each fraction. For risk characterization based on surrogate chemicals for each fraction, a hazard quotient (HQ) was calculated for each TPH fraction and a TPH Hazard Index was calculated as the sum of the individual HQs.

Details of the fraction approach are provided in Conceptual Site Models and Investigative Strategies, Human Health Risk Assessment, and Risk Calculators.

A survey has been conducted to identify the range of regulatory approaches used across the United States to evaluate TPH risk at petroleum release sites. This survey identified the range of regulatory approaches used across the United States. The findings of the States Survey are summarized in Appendix C.

2.4 TPH Risk Characterization Framework

Figure 2-4 illustrates the TPH risk characterization and evaluation framework recommended in this guidance. This framework presents principles and/or concepts for use when characterizing risk posed by surface and subsurface hydrocarbon releases to soil, air, groundwater, or surface water. The site characterization and risk calculation approach described in this document is directed toward characterizing the nature, extent, and risk posed by petroleum-contaminated soil source areas and the vapor phase and dissolved-phase plumes emanating from the contaminated soil source areas.

Figure 2-4. TPH guidance decision framework.

▼*Read more*

The decision framework identifies critical activities that are conducted in a stepwise fashion and others that are considered throughout multiple steps in the TPH risk characterization process. Activities that are considered throughout the process include:

- Regulatory Framework
- TPH Fundamentals (including chemical and physical properties)
- Updating the conceptual site model, in an iterative process, as data are collected or risk characterization assessments are completed
- Stakeholder Concerns

The stepwise process consists of the following actions:

1. If emergency response activities are warranted for a site, then these should be implemented prior to data collection for assessment of chronic risks/hazards and corrective action planning.
2. A preliminary conceptual site model (CSM) should be developed based on an initial survey of the site. This CSM will be used to develop the site investigation strategy and should be updated throughout the remediation, risk evaluation, and closure life cycle stages.
3. The site investigation should be conducted to assess the vertical and horizontal distribution of petroleum-related contaminants at the site and collect data necessary for risk characterization. However, in some cases, data may have already been collected. Multiple phases of environmental investigation may be necessary to collect data of known quality needed for risk characterization and corrective action planning.
4. The risk characterization step consists of an assessment of human health risks, ecological risks, and other factors considered in risk-based decision making (i.e., regulatory requirements, aesthetic criteria, or safety assessment). Various tools (i.e., calculators) are available that can quantify site-specific TPH risk calculations that may be used in the risk characterization process.
5. The risk characterization results are used to assess risk management and corrective action needs (e.g., remedial actions, engineering/institutional controls) or if site closure is appropriate.

The corrective action planning that may entail remediation and/or engineering/institutional controls should be implemented, as appropriate. Note that these aspects are beyond the scope of this guidance; the reader is directed to other ITRC or state guidance for reference.