6 Human Health Risk

This section discusses the evaluation of TPH at petroleum-contaminated sites to characterize human health risks. It also presents a discussion of the varying approaches to evaluating health risks for TPH, how the approaches need to be modified to address specific exposure routes, and how evaluation of metabolites and degradation products can be addressed. The discussion of how TPH risk assessment differs from the risk assessment of other chemicals and the variations in approaches to TPH risk assessment will serve as a basis for understanding and performing TPH risk assessment at individual petroleum release sites and can provide a basis for developing or revising regulatory approaches to human health risk assessment for TPH.

6.1 Introduction

Several methods are available for evaluating the human health risks associated with petroleum releases. One approach is estimating health risks for individual hydrocarbon compounds (e.g., BTEX, PAHs), and summing the risks and hazard indices estimated for each of the hydrocarbon chemicals evaluated. Such evaluations often address nonhydrocarbon components of the original mixture (e.g., additives such as MTBE) and help to estimate the cancer risk because TPH is not considered to be a carcinogen. These chemicals frequently make up a very small fraction of the bulk of the petroleum compounds for a release, which leaves uncertainty as to the health risk of the remaining mass. To address this issue, methods have been developed over the past twenty years to more precisely quantify TPH in terms of a small number of targeted, aromatic and aliphatic carbon ranges. Representative physiochemical constants and toxicity factors are then assigned to carbon ranges. This allows the data to be considered in standard risk assessments and related models in the same manner as is done for individual chemicals. Evaluating the human health risks associated with petroleum releases is the subject of ongoing research.

There are unique aspects of TPH that pose challenges when performing the risk assessment and interpreting the results. Three of the most important aspects of TPH that must be considered include the complex and variable nature of petroleum releases, the fact that the composition of any given released petroleum mixture can change substantially as a result of “weathering,” and the potentially substantial and selective partitioning of mixture components as they move from one environmental media into another. Over the last several years, regulatory concentration limits for TPH have evolved from being predominantly based on nuisance (e.g., odor, discoloration) to being increasingly based on human health protection Tomlinson and Ruby 2016. However, aesthetic considerations in addition to risk may need to be factored into environmental management decisions (see Case Studies).

Disturbance of heavily contaminated soil or groundwater during remediation and construction activities can also lead to the temporary but significant emissions of petroleum vapors and short-term risk to workers and occupants of neighboring properties. However, health effects are normally transient (temporary), and may quickly diminish once exposure is ceased. Methods to predict and manage shorter term risks are qualitatively discussed in Section 9 of this document.

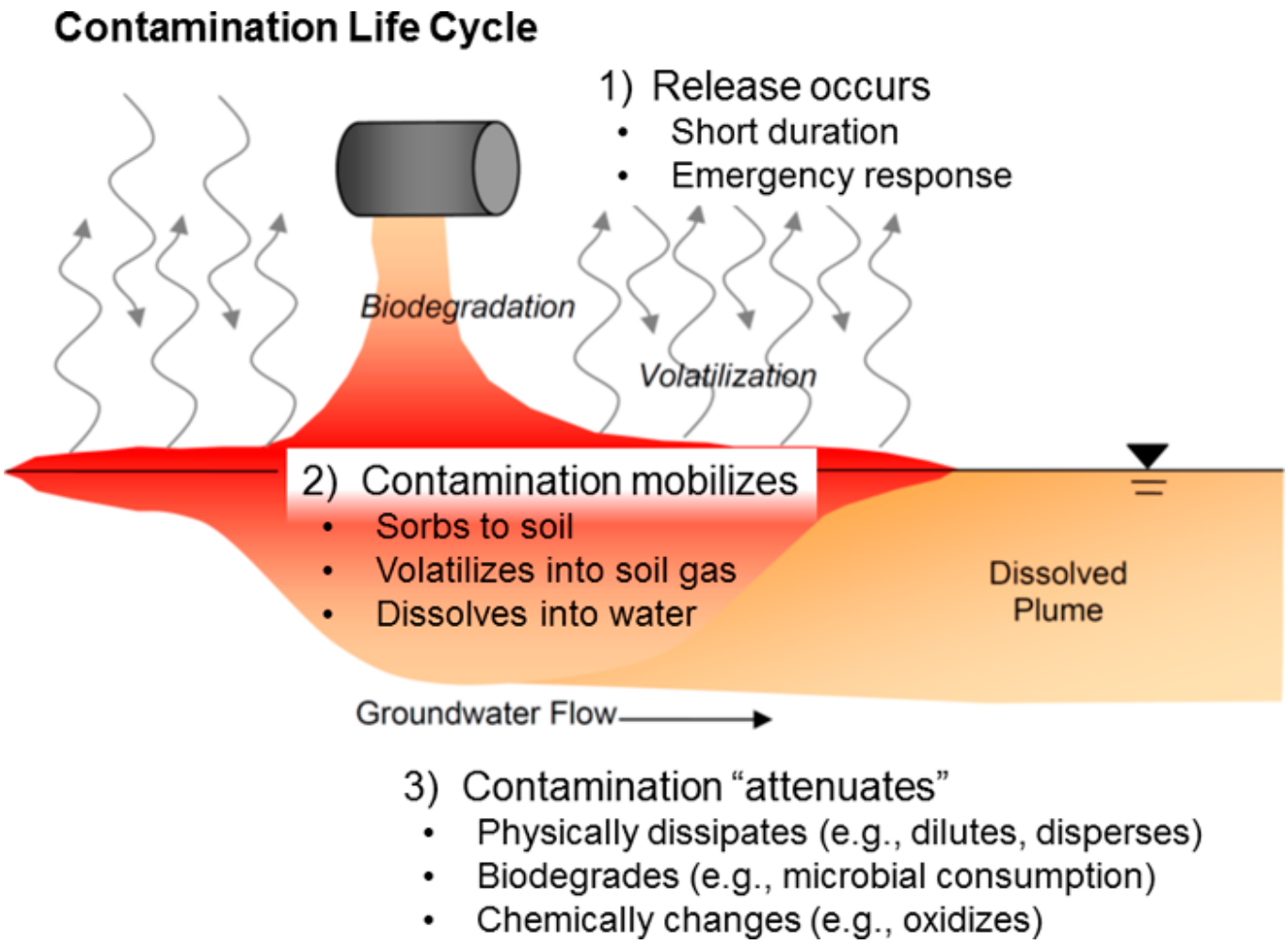


Figure 6-1. Contamination life cycle.

Petroleum mixtures reported as TPH can consist of thousands of individual compounds, and mixtures reported as a specific petroleum product (e.g., gasoline) can have significantly different molecular compositions. Even greater variability can be expected for petroleum releases of crude or residual oil, and it is not unusual to have more than one refined product present at a release site. Not only is the originally released material at virtually all petroleum release sites a complex mixture of hundreds of hydrocarbons, but the composition of nominally similar materials (i.e., gasoline, crude oil, etc.) can differ in ways that would affect the environmental mobility and toxicity of the mixture (see Petroleum Chemistry and Refining).

Once released into the environment, chemical and biological processes will begin changing the composition of the originally released material. Although such "weathering" of released petroleum has long been recognized, the need to explicitly consider the chemical and biological degradation products in a human health risk assessment is a relatively recent development.

Most or virtually all of the mass of degradation products typically results from the oxidation of hydrocarbons. Accordingly, the degradation products tend to be dominated by polar compounds that have different chemical properties and behaviors in the environment and different toxic properties than their parent hydrocarbons. These degradation products are commonly referred to as metabolites, and largely for the sake of convenience, that term is used in the text below. Consideration of the metabolites is important because, while they are not necessarily present at all sites, they can make up the dominant mass of the residue from a petroleum release during specific phases of the lifecycle of the release (see Alterations of Petroleum Mixtures in the Environment through Weathering Processes).

A consideration in evaluating health risk is the fact that various constituents of TPH will tend to differentially partition from the main mass of a fresh or weathered release if they move from one environmental media to another. Surface water or groundwater affected by a petroleum release would be enriched in the more water-soluble constituents relative to the mixture that may have been released to soil, for example. Vapor intrusion is only likely to involve the more volatile constituents. Plant or fish uptake would also involve selective enrichment.

Some environmental media may not be amenable to TPH analyses. Concerns about health risks posed by accumulation of chemicals associated with a petroleum release in irrigated crops or fish or animal tissue could not be addressed by chemical analyses for TPH because the petroleum-related materials could not be distinguished from the plant or animal tissue. The risk assessor would need to decide on a set of appropriate indicator chemicals for such evaluations.

6.2 Exposure Assessment

Key factors to consider when assessing TPH exposures include the wide variation in physical and chemical properties of the mixture and potential exposure impacts as the mixture partitions between different environmental phases. Estimating exposure point concentrations in different media requires characterizing the TPH fractions (if a fraction-based approach is being used), individual chemicals, or both, that will be the basis of an evaluation. Any site-specific needs would also need to be considered, as would any applicable regulatory requirements or guidelines. Site-specific needs may also include consideration of acute effects and aesthetics (e.g., odor or visual impacts) (see Examination of Risk-Based Screening Values ITRC 2005, and Use of Risk Assessment in Management of Contaminated Sites ITRC 2008).

6.3 Direct Contact with TPH

Appropriate sampling and analysis methods for TPH in soil are presented in Section 5. The sampling methods need to consider the type of petroleum product, whether the product is new or weathered, and other environmental conditions (e.g., heat) that could affect the selection of complete exposure pathways or the quantification of exposure.

Direct contact with chemicals in soil typically involves ingestion, dermal contact, and inhalation of vapors or particulates USEPA 2017c. To evaluate these potential exposure pathways for a TPH risk assessment, the composition of the TPH mixture should be considered. For the ingestion and dermal contact pathways, bioavailability of TPH compounds may be considered. Although bioavailability methods for PAHs are not yet defined, the potential for refining the human health risk assessment (HHRA) may be considered. The use of bioavailability in risk assessment is discussed in the ITRC's Bioavailability of Contaminants in Soil (BCS) document. Though the BCS document does not specifically discuss TPH, it presents methods for evaluating oral and dermal PAH bioavailability that can be applicable to TPH if individual PAHs are included in the HHRA. The BCS also discusses the considerations (e.g., PAH source and concentration, or skin models) for validating these methods and identifying other methods that can predict bioavailability with higher certainty.

For some TPH mixtures containing PAHs, dermal contact may contribute to the overall cancer risk USEPA 2018c. However, caution must be used when considering PAH dermal risk assessment because the EPA has not finished evaluating dermal toxicity data to develop appropriate dermal cancer toxicity values. In addition, methods have not been developed for the evaluation of direct contact with petroleum products based on total TPH (DRO/GRO) or TPH fractions. Currently, EPA has provided chemical-specific dermal absorption efficiency factors (referred to as AEd) for some TPH volatiles, and semivolatiles are assigned a default value of 10% USEPA 2004. EPA is continuously updating the dermal absorption values as information becomes available USEPA 2018c.

6.4 Soil to Ambient Air Exposure to TPH (Volatiles and Particulates)

Soil to ambient air inhalation exposure to TPH volatile components is commonly evaluated for individual TPH compounds (e.g., BTEXN and PAHs) using mathematical models, e.g., the Jury model Jury, Farmer, and Spencer. 1984, which predicts chemical transport and requires single-chemical data input (HLC, K_{ow}, K_{oc}), and dispersion models (AERMOD), which predict subsequent dispersion of vapors in ambient air. The Jury model does not accommodate mixtures USEPA 1996, 2002. However, where physiochemical property data and inhalation toxicity values are available for individual TPH fractions MADEP 2003, the Jury model can be used to estimate the flux for specified carbon ranges and the risk can be evaluated for specific carbon ranges. The risk to exposure to total (bulk) TPH can also be evaluated using weighted averages of the estimated risk for individual carbon fractions Brewer et al. 2013. It should be noted that exposure evaluation based on the Jury modeled flux cannot be used for evaluating soils when the TPH mixture is present as a free-phase product (saturated concentration) USEPA 2002.

Alternative methods for evaluating ambient air exposure to individual carbon ranges in soil that are used in many states include soil vapor and direct flux measurements. Direct flux measurements using flux chamber sampling are combined with dispersion modeling to estimate air concentrations that are then compared to ambient air screening levels of individual

compounds or petroleum hydrocarbon mixtures USEPA 2002; ITRC 2008.

For particulate emissions of TPH in soil, the particulate emission factor (PEF) can be used, which is applicable to all types of TPH compounds, because it is not chemical-specific. At sites with increased soil-based activities (e.g., construction sites), the particulate emissions due to vehicular traffic on unpaved roads should be considered in the PEF derivation USEPA 2002; ITRC 2008.

6.5 Leaching from Soil to Groundwater

As discussed in Sections 5.3 and 5.4, physiochemical constants assigned to individual carbon ranges can be used in soil leaching models to derive leaching-based screening levels or predict groundwater concentrations resulting from soil migration to groundwater in the same manner as carried out for individual compounds. To estimate the potential for TPH mixtures to leach to groundwater, it is important to incorporate appropriate chemical-specific values (HLC, K_{oc}) specific to each TPH fraction USEPA 1996. The accuracy of commonly used leaching models is dependent on site-specific parameters and adequate knowledge of the physio-chemical properties of the contaminant(s). This can be particularly challenging for complex mixtures such as TPH. Further research regarding this subject is required.

In general, the potential for leaching will be greatest for the <C9 aromatics and other compounds with high aqueous solubility (e.g., TPH polar metabolites). The leaching potential of polar metabolites has yet to be evaluated. Identifying and incorporating mole fractions of the petroleum hydrocarbon mixture into the leaching evaluation is essential. Failure to include TPH fractions in this pathway's evaluation can result in inaccurate estimates of release from soil and transport into the water phase, which may be amplified when (1) the TPH mixture is present as LNAPL; or (2) the petroleum hydrocarbon mixture contains heavier oils (higher molecular weight compounds) with negligible aqueous solubility.

Analytical tools used to empirically determine TPH leaching potential include the Synthetic Precipitation Leaching Procedure (SPLP) analysis (EPA SW-846 Method 1312) and the SPLP Batch Test Leaching Model, which both use a slightly acidic extraction fluid to estimate leachate concentrations in situ.

If LNAPL is present in soil, leachate analyses may inaccurately predict the leaching potential of the TPH mixture due to direct partitioning of nonsorbed droplets into the leachate solution. One option to help minimize this uncertainty is the use of soil column leaching tests. See Case Studies 1, 2, 3, and 5 for more information. Note that polar metabolites can form in the vadose zone as hydrocarbons migrate.

6.6 Exposure to Groundwater/Surface Water

Petroleum spills and leaks to land surface or surface water bodies can result in elevated concentrations of TPH and TPH-related metabolites in groundwater or surface water via the migration of free product or leaching. Short-term (subchronic) and long-term (chronic) exposures to TPH can occur via contact with groundwater used as a potable water supply (e.g., private drinking water wells) and other water uses (e.g., swimming pools). TPH presence in groundwater can be detected by affected receptor populations from the distinctive taste, discoloration, and odor characteristic of some of the individual TPH components (e.g., benzene).

Due in part to the complexity of TPH components themselves, determining their potential exposures becomes a challenge. The exposure point concentration is heavily dependent upon the specific analytical method details and requirements, which vary from state to state. Over the years, the selection of surrogate or indicator compounds (or a combination of compounds) to represent TPH has become a common remedy to this problem.

Exposure to surface water may be lower than that of groundwater due to generally less frequent contact and shorter term average exposures or shorter average exposure durations. In instances where TPH-contaminated groundwater may be discharging to a surface water body, some states allow use of surface water modeling and site-specific dilution factors for high flow, lentic systems to predict TPH concentrations in surface water. Other state agencies, such as MADEP, have issued policy in the form of a support document on the VPH/EPH approach to modeling MADEP 2002b.

A number of challenges exist when investigating and addressing the risk from exposure to fuel-related chemicals in surface water bodies (e.g., rivers, creeks, sensitive wetlands, drainage canals, ditches, roadway runoff, etc.) that may be flowing or discharging to other locations. One issue is the presence of competing sources; the collection of background data can be critical in eliminating these other sources. In addition, some surface waters (e.g., small wetlands) may have normally high

background concentrations of nonpetroleum-related compounds detectable in the TPH analysis that must be distinguished from potential sources in question. High background levels may come from either naturally occurring sources (e.g., natural seeps) or anthropogenic sources. Environmental forensics could help in making this distinction between the footprint of TPH in background material and TPH from a particular source.

6.7 Exposure to Air

6.7.1 Outdoor (Ambient Air)

Inhalation toxicity factors assigned to individual carbon ranges can be used to develop risk-based screening levels for ambient air and/or directly quantify human health risk in the manner as done for individual compounds. Exposure assessment of TPH and TPH-related compounds in ambient air resulting from emissions from contaminated soils can be complicated and, in many cases, irresolvable in the presence of multiple (non-site-related) sources of TPH in ambient air, including fueling stations, auto exhaust, cleaning fluids, and other uncertain and nonpoint sources. Because of these potentially confounding sources, it may be important to include sufficient background (or reference) locations in any outdoor air TPH sampling program, if ambient air exposure is to be measured directly. The alternative to direct measurement, modeling of ambient air concentrations from soil, is discussed in Section 6.4

6.8 Food Chain

Due to the limited studies, bioassays, and heightened uncertainty in the bioaccumulation and biomagnification of TPH in aquatic and terrestrial ecosystems, these evaluations are typically not recommended for use in risk management decision making. Instead, individual chemicals of concern become the focus. In general, the lower molecular weight aliphatics and aromatics do not bioaccumulate, but there is some evidence that aquatic and terrestrial organisms do bioaccumulate some TPH constituents, particularly PAHs Farrington et al. 1982. However, depuration does occur if the source of the contamination is removed Cox et al. 1975; Williams et al. 1989.

Some of the difficulties associated with trying to evaluate the food chain uptake pathway include the following:

- terrestrial plants and aquatic algae can metabolize hydrocarbons, making it difficult to decipher whether the hydrocarbons in the soil will actually be in the plants from the soil Eisler 2000
- plants and animal tissues are made up of organic chemicals, which will often themselves report as TPH if analyzed Hoffman et al. 2003
- models can attempt to predict only what could actually occur (e.g., use of food chain models that estimate uptake may not truly reflect what is actually happening). Similar arguments can be applied to the animal meat uptake pathway (see Ecological Risk Assessment).

6.8.1 Plant Consumption

Humans may be indirectly exposed to TPH via plant ingestion in instances where food crops are irrigated with water containing TPH, for example. However, because TPH analytical methods would extract plant material as well as any petroleum components, they cannot be used to analyze for petroleum residues in plants. Risk assessment of TPH in plant material must rely on chemicals selected to match the surrogate chemicals of potential concern in the soil or irrigation water to which the food crops may have otherwise been exposed. Further information on plant uptake of TPH and TPH toxicity in plants is provided in Ecological Risk Assessment.

6.8.2 Meat and Milk Consumption

Human exposure to TPH may also occur through the ingestion of livestock (e.g., contaminated meat) or consumption of milk from animals that may graze on TPH impacted soil or ingest TPH-contaminated water as drinking water. As with plant consumption, TPH analytical methods are not applicable to meat or milk. Indicator chemicals relevant to the spilled petroleum that would be expected to partition into and possibly accumulate in the edible portions of the target species need to be selected.

6.8.3 Fish and Shellfish Consumption

Consumption of fish and other aquatic organisms following a fuel release or crude oil spill into surface water is an exposure scenario that often needs to be addressed. Fisheries may be closed as a preventive measure following a spill, and a human health risk assessment may be required before the fishery can be reopened. As with plant and other animal tissues,

predicting or measuring the uptake of hydrocarbons into fish tissue from a specific petroleum release is challenging. Chemical analysis of fish and shellfish using fractionation or a bulk TPH method is not practical because fish oil and other tissue components will be detected as TPH. Rather, indicator chemicals relevant to the spilled material that would be expected to partition into fish and shellfish need to be selected Yender et al. 2002; CAOEHHA 2015. In addition to a human health risk assessment, it may be necessary or desirable to perform a sensory evaluation (i.e., testing for off-flavors and off-odors) of the fish and shellfish in support of a decision to reopen a fishery Reilly and York 2001. Although analytical instrumentation is becoming more sophisticated, these instruments are chemical detectors only and are incapable of making any sensory judgment on odor or flavor NOAA 2001.

6.9 Toxicity Assessment

Equally important as exposure assessment in risk evaluation is the understanding of toxicity. The section below presents some focused background points for the discussion of the toxicity assessment of TPH along with a discussion of the basic approaches that have been taken to the toxicity assessment of TPH. The challenges and proposed approaches to evaluating the toxicity of petroleum metabolites are also discussed.

6.9.1 Background and Overview of TPH Toxicity Assessment Methods

There are a few basic approaches to toxicity assessment for TPH. Each approach addresses the challenges posed by the assessment of TPH toxicity in a different way. The best approach to apply in any given situation, however, is often a hybrid approach, particularly if multiple exposure routes need to be addressed.

▼*Read more*

The most basic challenge to evaluating the toxicity of TPH in a human health risk assessment is the fact that any given TPH mixture can consist of hundreds to thousands of different compounds. Even if it were possible to measure the concentration of each compound, toxicity data are not available for each one. Another challenge is the fact that petroleum mixtures released to the environment will change as they weather. Even if there are results from toxicity testing of a fresh petroleum product, weathering will change the composition of the mixture to such an extent that toxicity results from fresh product cannot be extrapolated to weathered product. In addition, there will typically be further change of mixture composition as a result of partitioning, if the released petroleum moves from one environmental media into another.

A few additional factors to keep in mind when selecting an approach for estimating the toxicity of a TPH mixture and when interpreting the results include: (1) the compounds making up any specific mixture analyzed as TPH can include hydrocarbons as well as polar compounds; (2) the mixture reported as TPH can include naturally occurring (e.g., humic acids) and anthropogenic substances (e.g., PCBs, chlorinated solvents, phthalates) that are not derived from released petroleum; and (3) the compounds detected and reported as TPH will depend on the specific TPH analytical method used (see TPH Fundamentals).

Two foundational concepts applicable to all health risk assessments that are important in evaluating the toxicity of TPH are the assumption of additivity of dose or effect and the closely related risk assessment policy generally referred to as “the mixtures policy.” The USEPA addresses the additivity assumption in their Provisional Peer-Reviewed Toxicity Values (PPRTV) document for Complex Mixtures of Aliphatic and Aromatic Hydrocarbons USEPA 2009d, and they recommend assuming additivity of effects of hydrocarbon fractions comprising TPH. The Agency for Toxic Substances and Disease Registry ATSDR 1999 also recommended assuming additivity when evaluating environmental levels of TPH.

As shown below, toxicity testing of certain highly refined hydrocarbon mixtures with narrow carbon size ranges (e.g., white mineral oil) has been applied to the toxicity of TPH fractions found in the environment with similar molecular size ranges. The assumption underlying this extrapolation is that the mixture of the narrow range of hydrocarbons subjected to toxicity testing is similar in composition and toxicity to the mixture of chemicals comprising the corresponding TPH fraction. Accordingly, toxicity test results from the similar mixture are presumed to be a reliable estimate of the particular TPH fraction.

Even though TPH is itself a mixture, it is present at contaminated sites among a few or many additional COPCs. Where aggregate risk evaluations of noncancer health risks for TPH and other COPCs are allowed, the Hazard Index (HI) calculated for TPH can simply be added to the HI calculated for other COPCs. For the evaluation of cancer risk, the typical approach taken for petroleum release sites is the same approach as is used for any other site risk assessment (i.e., TPH is not generally considered to be a carcinogen so the lifetime incremental cancer risk is estimated for individual carcinogenic

chemicals and summed).

The discussion of toxicity assessment for TPH presented below focuses on methods for evaluating chronic exposures, but acute exposure can also be a concern for TPH releases. Information relevant to addressing acute exposures to the public and in the workplace has been provided most directly by the ATSDR, the Occupational Safety and Health Administration (OSHA), and the National Institute for Occupational Safety and Health (NIOSH).

▼*Read more*

To address the concerns that community members and other stakeholders may have about acute toxicity of the refined petroleum products, ATSDR 1996 offers a frequently asked questions (FAQ) section for automotive gasoline, stating that inhaling or ingesting large amounts of gasoline is irritating to the lungs or stomach lining, respectively. Breathing or swallowing large amounts of gasoline may cause harmful effects on the nervous system, ranging from serious effects like coma or inability to breathe, to less serious effects like dizziness and headaches. Comments on OSHA's 1989 Final Rule on Air Contaminants Project may be valuable for addressing both public and workplace exposures, and they suggest that people exposed to 160–270 ppm of gasoline for several hours may experience eye and throat irritation, but no symptoms of narcosis OSHA 1989. ATSDR 2017 also offers toxicological information regarding jet fuels (JP-5, JP-8, and jet A fuels).

Though little is known about its effects on human health, ATSDR 2017 notes that humans who have ingested kerosene, a fuel similar in composition to the jet fuels, reported harmful effects on the respiratory tract (cough and difficulty breathing), gastrointestinal tract (abdominal pain and vomiting), and nervous system (drowsiness, restlessness, and convulsions). Given the variable nature of gasoline composition, OSHA does not have occupational exposure limits for gasoline. However, OSHA 2012 has set a time-weighted average permissible exposure limit for petroleum distillates (naphtha) at 500 ppm (2,000 mg/m^3).

6.9.2 Approaches to TPH Toxicity Assessment

Recognizing the challenges posed by the need to characterize the toxicity of TPH, a variety of approaches have been developed and are currently in use. The oldest approaches rely primarily on an evaluation of indicator chemicals, which may or may not have been accompanied by an evaluation for various whole product fractions (e.g., gasoline range total petroleum hydrocarbons, diesel range petroleum hydrocarbons, or residual range total petroleum hydrocarbons). More recently, a variation of the indicator chemical approach has evolved, in which the bulk TPH mixture is divided into its aliphatic and aromatic components and then into discrete carbon ranges smaller than that of a typical petroleum product. The potential toxicity of these fractions is then used to evaluate risk, generally in conjunction with an evaluation of selected individual hydrocarbon chemicals. These general approaches are illustrated in Figure 6-2, which is from the TPHCWG 1999.

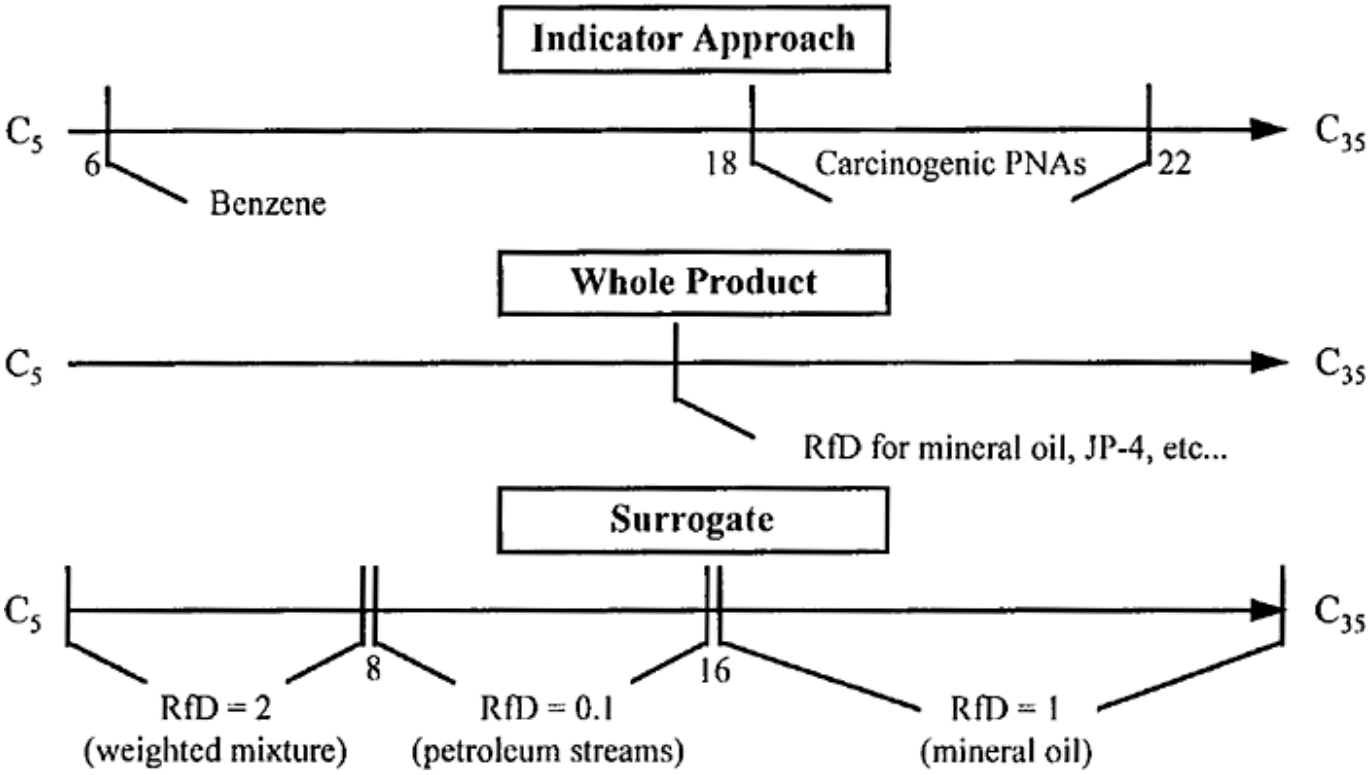


Figure 6-2. TPH toxicity assessment methods TPHCWG 1999**.**

The three basic approaches to toxicity assessment of TPH are described below, including the indicator chemical approach, the fractionation approach, and whole product approach. Although each of these basic approaches are distinct, they are most often used in conjunction with each other (see TPH Fundamentals).

6.9.2.1 Indicator Chemical Method

One approach to evaluating health risks for petroleum hydrocarbon mixtures is to rely on indicator chemicals USEPA 1986, 1989, 2000c. Local guidance can vary for the indicator chemicals to be used for either cancer or noncancer health risks. The results of the States Survey show the indicator chemicals recommended by several different states.

The assumption underlying the use of the indicator chemical approach is that the indicator chemicals represent most of the mixture's toxicity, and therefore, the health risk of the entire mixture can be estimated to a reasonable degree of certainty by relying on the health risks estimated for the indicator chemicals USEPA 1989. Contrary to this assumption is the fact that the indicator chemicals often make up a small fraction of the mass of the TPH range to which they are applied. On the other hand, the indicator chemicals are thought to be more toxic than the rest of the chemicals in the mixture. Concern over the validity of the indicator chemical approach is most often raised for sites with weathered releases of products where the indicator chemicals used for the released product(s) may not be present at detectable levels, but at which residual hydrocarbons are noticeably or measurably present. In such cases, reliance on indicator chemicals alone can cause health risks to be underestimated or can leave questions about the adequacy of an evaluation relying solely on indicator chemicals.

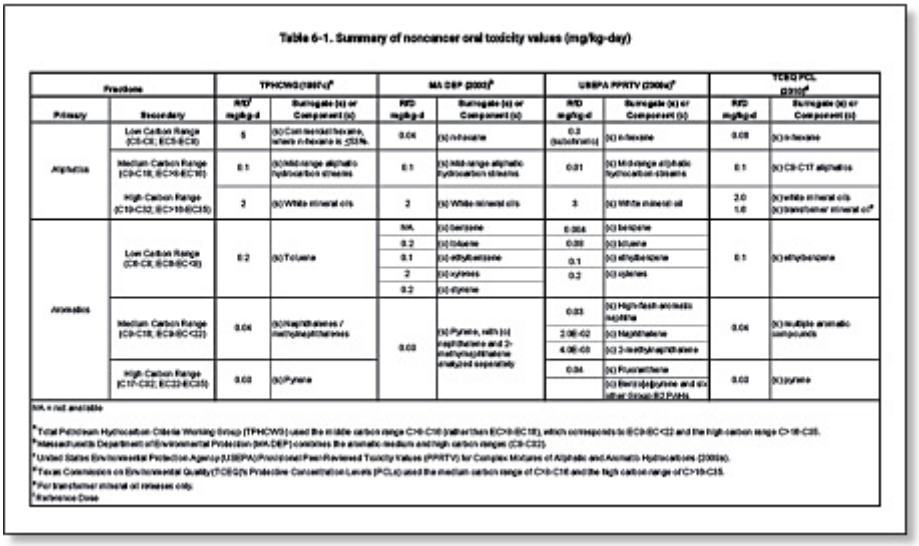
▼*Read more*

The need to evaluate health risks for TPH residues in cases where the evaluation of indicator chemicals alone results in very low or zero health risk can be driven by regulatory requirements, community stakeholders, the need to adequately characterize site contamination, or by risk communication needs, particularly in cases where the indicator chemicals may be perceived to be underestimating risk. In such cases, reliance on the indicator chemicals alone can cause exposure and risk to be underestimated, particularly if unresolved hydrocarbon mixture and/or polar metabolites make up a large fraction of the mass of material present. Some states indicated in the States Survey that they believe an indicator chemical only approach adequately characterizes health risks. The survey did not ask the states for data or other information to support this conclusion and none were available at the time this document was published.

6.9.2.2 Fractionation Methods

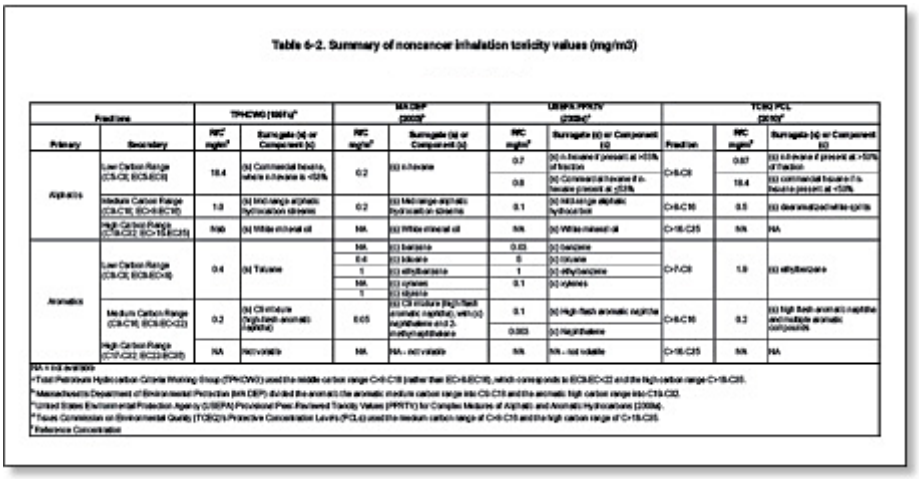
Under the fractionation approach TPH is divided into aromatic and aliphatic compounds, and the aromatic and aliphatic compounds are further divided into several defined carbon ranges. The various fractions were originally divided into groups that would have similar fate and transport properties MADEP 1994, 2002a; TPHCWG 1997a. Massachusetts MADEP 1994, British Columbia BCMoE 1995, and the TPHCWG 1997a were the earliest groups to develop and recommend use of the fractionation approach. The ATSDR 1999, USEPA 2009d, and several states have also adopted versions of the fractionation approach. Examples of fractions and the toxicity factors assigned to them are shown below in Tables 6-1 and 6-2. Variations in the fractionation approach include different divisions of the fractions to be addressed and different approaches to the assignment of a toxicity value to each fraction (e.g., assign the toxicity of a constituent typical of the toxicity of the fraction or assign the toxicity of the most toxic constituent).

Table 6-1. Summary of noncancer oral toxicity values (mg/kg-day)
TPHCWG 1997c; MADEP 2003; USEPA 2009d; TCEQ 2010



View Table 6-1 in Adobe PDF format.

Table 6-2. Summary of noncancer inhalation toxicity values (mg/m3)



View Table 6-2 in Adobe PDF format.

▼*Read more*

As noted by the TPHCWG 1997a, the fractionation approach was intended to supplement the indicator chemical approach to evaluating TPH. It provides a way to address the situation noted above, in which indicator chemicals are not present at detectable levels, yet petroleum residues requiring evaluation are present. The fractionation approach also has the

advantage of flexibility, as it can be applied to any TPH mixture found in the environment, and it results in a greater characterization of the site and risk posed by TPH.

When performing human health risk assessment using the indicator or individual chemical approach, each TPH fraction is treated as though it were a separate COPC. Hazard quotients (HQs) for individual TPH fractions are added to HQs for other TPH fractions and to HQs for TPH indicator or individual chemicals to estimate an HI for TPH.

When performing this calculation, it is important to subtract the concentration of individual chemicals from the concentration for the TPH fraction that would have included the individual chemicals. This exercise is to avoid double counting the concentration of TPH and individual chemicals. Depending on how the TPH fractions are defined, these chemicals may account for most, if not all, of a fraction. For example, BTEX could add up to all of the small aromatic hydrocarbon range, C6–C8, in the USEPA 2009d fractionation approach. This should be done only where the TPH and individual chemicals have been analyzed using the same method. Many labs will perform this subtraction for you.

Although the organizations mentioned above have adopted or recommended TPH fractionation as the preferred way of addressing human health risk assessment for TPH, there are differences in the carbon ranges and toxicity factors recommended by these organizations for each carbon range (see Table 6-1). Differences in the recommended toxicity factors stem, in part, from the use of different approaches to selecting the toxicity factors for each TPH fraction.

The approaches used include:

- use of toxicity test results from a hydrocarbon mixture similar to a particular aliphatic or aromatic fraction
- selection of toxicity factors for one or more indicator chemicals to represent the toxicity of the mixture making up a fraction
- a hybrid approach, in which both individual chemicals and toxicity test results from a similar mixture are presumed to be a reliable estimate of a particular TPH fraction USEPA 2009d. A variety of toxicity factors have been applied to similar fractions by the various organizations that have recommended fractionation approaches.

Differences in recommended toxicity factors are attributable to a variety of factors, including:

- availability of new toxicity studies since the approach was first developed
- updated toxicity evaluation methods
- better understanding of the toxicity of the TPH components
- procedural and policy differences between the various organizations in selecting toxicity values
- changes over time in the procedures and policies related to setting toxicity limits
- differences in judgment regarding the most appropriate test results or critical study and the application of uncertainty factors

The USEPA 2009d noted that the toxicity factors they have developed for the six aliphatic and aromatic hydrocarbon fractions are Provisional Peer-Reviewed Toxicity Values (PPRTVs), which means they have been developed using the similar methods, data sources, and guidance as are used for developing toxicity factors for the USEPA Integrated Risk Information System (IRIS) Program. PPRTVs are developed specifically for use in the Superfund Program and receive peer review by two USEPA scientists and their independently selected scientific experts. They are not subjected to the same multiprogram peer review to which IRIS values are subjected USEPA 2009d.

As shown in Table 6-1, the toxicity factors used to develop the USEPA Regional Screening Levels (RSLs) for TPH include PPRTVs for TPH fractions, as well as IRIS values selected as surrogate toxicity factors for TPH fractions USEPA 2018c. For at least some carbon range fractions, the values used in the derivation of the RSLs are more conservative than the PPRTVs recommended for the same fraction. Although no specific explanation for the difference is offered in the RSL documentation, the RSL Work Group selected the most toxic individual chemical as the surrogate for the toxicity of specific hydrocarbon fractions. Because the RSLs are intended for use as screening values, it would be consistent with standard risk assessment procedures to use less conservative toxicity factors, such as PPRTVs, for a baseline risk assessment or for the calculation of risk-based cleanup values, for example.

Although cancer risk for petroleum releases are almost always based on estimating and summing cancer risk for carcinogenic individual chemicals, the USEPA 2009d did develop inhalation unit risk (IUR) factors for their low carbon range aliphatic (C5–C8, EC5–EC8) and medium carbon range aliphatic (C9–C18, EC>8–EC16) TPH fractions as part of its PPRTVs for Complex Mixtures of Aliphatic and Aromatic Hydrocarbons. USEPA characterizes these IUR factors as “screening level” values that may be useful in “certain situations” and recommends reporting the fraction of any estimated cancer risk that is

attributable to these more uncertain toxicity factors. As discussed in FAQ#48 in the RSL USEPA 2018e documentation, the RSL Work Group elected not to use the screening level IURs in the derivation of the RSLs because they felt that combining cancer risks based on these TPH fractions and individual chemicals would be overly protective.

As new toxicity data become available, it will be necessary to consider updating the toxicity factors assigned to the various TPH fractions, and the policies used by one agency to select a toxicity factor may not be appropriate for another agency. Agencies setting up new programs for evaluating TPH based on TPH fractions may want to consider the availability of toxicity data more recent than the last toxicity factors adopted by another agency and may want to evaluate the appropriateness of the policies underlying another agency's toxicity factors. For example, a report sponsored by the American Petroleum Institute ToxStrategies 2016 noted that newer toxicity studies than those relied on by the USEPA 2009d were available, and that the size of the uncertainty factors used in the derivation of some toxicity factors by USEPA 2009d was larger than those applied to the same toxicity studies by other organizations.

6.9.2.3 Whole Product Method

Under the whole product approach, a single toxicity factor is assigned to a whole petroleum product, such as gasoline, diesel fuel, jet fuel, bunker fuel, crude oil, etc. A variety of approaches may be used to assign the toxicity factor for the product. For example, toxicity test results from testing a whole product might be used. The primary drawback to this approach as discussed above is the fact that the composition and toxicity of the product will change as it weathers and could only be applied to fresh releases. Another important consideration is the higher degree of variability in the unrefined petroleum materials (e.g., bunker fuel and crude oil), which would pose a great deal of uncertainty in extrapolating toxicity test results from one tested product to others. In addition, test results are not available for all of the whole petroleum products.

Because whole product TPH analytical results are frequently a significant portion of, if not the only TPH data available for a site, one can be faced with having to evaluate health risk for such reported mixtures. Although a variety of approaches can be used to assign toxicity factors to whole product carbon ranges, appropriate regulatory guidance on the topic should be consulted for recommended approaches. The most technically defensible approach is arguably to make assumptions about the proportions of TPH fractions comprising the released petroleum mixture and use recommended toxicity factors and chemical constants for the assumed fractions. While this approach may be the most technically defensible, it nonetheless entails more uncertainty than is associated with health risk estimates based on measured TPH fraction data. Use of this approach allows at least a screening level evaluation of whole product data. Two agencies have published guidelines for this method of evaluating health risks for whole product TPH (e.g., GRO, DRO, RRO) CASWB-SFBR 2016a; HIDOH 2017.

The whole product method of evaluating the toxicity of TPH entails more uncertainty than is associated with health risk estimates based on measured TPH fraction data. It can have value as part of a screening level evaluation, but should be used with great caution, if at all, for human health risk assessments. Local guidance should be consulted before using a whole product method for evaluating the toxicity of TPH.

6.10 Evaluating Toxicity of Polar Metabolites

This section discusses the challenges to evaluating the toxicity of the polar metabolites and the approaches that have been proposed for addressing the challenges.

6.10.1 Challenges in Evaluating the Toxicity of Polar Metabolites

It is well established that hydrocarbons (and other chemicals) undergo "weathering" (see Alterations of Petroleum Mixtures in the Environment through Weathering Processes) in the environment. Understanding the toxicity of the resulting hydrocarbon degradation of products is important because the majority, if not all, of the hydrocarbons at a petroleum release site can be present in soil or groundwater in the form of polar metabolites. Although much, if not all, of the mass of the metabolites can degrade to carbon dioxide and water eventually, the polar residues can be the source of ongoing potential or actual exposure for varying periods of time after a release. Accordingly, explicit evaluation of the metabolites may be warranted when they are present.

▼*Read more*

The same fundamental challenges of a variable and changing mixture of chemicals with sparse toxicity data on the mixtures and/or components of the mixtures that apply to the hydrocarbons at petroleum release sites also apply to the polar metabolites. In fact, the degree of uncertainty associated with understanding the chemical composition of the polar

metabolites and with understanding the toxicity of polar metabolite mixtures is even greater than for the parent hydrocarbon product mixtures. The technical and practical challenges associated with a definitive characterization of the polar metabolites are such that one will never have definitive characterization of the chemical composition of the mixture at any given site.

Estimating health risks for the metabolites at petroleum release sites will require assumptions about the chemical composition and the toxicity of the mixture present and will entail at least as much uncertainty as is associated with estimating health risks at sites with releases of other chemical mixtures. The chemistry of petroleum degradation products is an active area of research and our understanding of it is likely to grow and change in the future.

As discussed in Section 4.4 the production of polar metabolites is largely the result of biodegradation, including both aerobic and anaerobic degradation processes. Chemical degradation processes (e.g., photooxidation) can also contribute to the natural attenuation process. Because polar compounds can be present in crude oil Meckenstock et al. 2014, they may be present as part of the released material at crude oil or residual oil release sites, as well as being the result of natural attenuation of hydrocarbons in these petroleum mixtures Thorn and Aiken 1998. It is important to recognize that polar compounds can also be present at a site in soil or groundwater as part of the natural background chemicals (e.g., humic acids) or from releases of other anthropogenic chemicals not related to the petroleum release. These are issues that can generally be addressed with a good conceptual site model, and the need to differentiate polar natural background substances from polar compounds may require devoting more resources to developing a more completed conceptual site model than would otherwise be the case.

It may be necessary to characterize natural or anthropogenic background sources of polar compounds at some sites prior to performing a human health risk assessment for petroleum releases. In some cases, such an evaluation is needed to allow an evaluation of the "release" separate from the evaluation of the background. Estimating the health risks associated with such background substances would require information on the concentration and toxicity of the background substances.

The polar metabolites that have been detected in at least some petroleum release site groundwater plumes consist almost entirely of oxygen-containing compounds derived from hydrocarbons CASWB-SFBR 2016b; Zemo, O'Reilly, et al. 2013; Zemo et al. 2017 that include alcohols, phenols, aldehydes, ketones, and acids/esters of dicarboxylic acids. At larger release sites, these plumes have been demonstrated to persist for decades and likely will persist much longer. The progression of metabolites through various classes of oxygenated species is well documented, but the mixture of constituents present at any given petroleum release site will be variable and will change with time Zemo et al. 2013; Zemo et al. 2017.

6.10.2 Approaches Proposed for Evaluating the Toxicity of Polar Metabolites

Two specific approaches for evaluating the toxicity of polar metabolites have been proposed. One assumes that the bulk polar metabolites have the same toxicity as the bulk hydrocarbons in the TPH fraction in which they are detected CASWB-SFBR 2016b. A second approach assigns toxicity factors for individual polar oxygenate degradation products to chemical structural families of degradation products Zemo, O'Reilly, et al. 2013; Zemo et al. 2017. Consideration of these approaches is discussed in the TPH case studies published by HIDOH 2018.

Both of these approaches are primarily intended to address refined middle distillate products in water. The focus on the middle distillate range is primarily because gasoline range organics are generally addressed by the evaluation of relatively water-soluble indicator chemicals (i.e., BTEX) and because polar metabolites of gasoline range hydrocarbons tend to have retention times in the middle distillate range. In addition, hydrocarbons larger than those in the middle distillate range from refined products have such low water solubility that they are not found dissolved in water at significant levels. One concern associated with both of these approaches is that the methods for measuring TPH-d will not always detect all of the polar compounds present in a sample and that the level of polar compound can be underestimated Bekins et al. 2016; Mackay et al. 2018.

▼*Read more*

However, residual fuels and crude oil may contain larger and different hydrocarbons (as well as other organic chemicals) than are present in refined products (e.g., PAHs, oxy-PAHs, sulfur compounds). These constituents may be metabolized by microorganisms in the environment to compounds that would be different than compounds present in releases of refined product Tissot and Welte 1984; Zemo and Foote 2003. Residual fuels and crude oils may also contain polar compounds that could be present in the parent spill material and that could be further metabolized. Thus, the range of chemical structures

and the range of molecular sizes of metabolites and degradation products in weathered residual fuels and crude oils will be different from the mixtures seen in weathered releases of refined products.

As noted above, one approach to evaluating the toxicity of polar metabolites assumes that the polar metabolites have the same toxicity as the hydrocarbons detected in routine extractable TPH analyses without a silica gel cleanup (SGC) step (e.g., TPH diesel and TPH motor oil or carbon range fractions). Under the similar toxicity approach TPH concentrations could be compared to screening levels developed for hydrocarbons or could be used in a risk assessment CASWB-SFBR 2016a, 2016b; HIDOH 2017. One practical advantage of this approach is that it does not require application of a sample cleanup step to remove polar compounds. (See Case Studies, Section 11 for additional discussion of metabolite toxicity and examples of implementation).

A second approach to evaluating the toxicity of the polar metabolites involves assigning toxicity factors to various fractions of TPH that are detected after silica gel cleanup and are assumed to consist of polar metabolites of hydrocarbons. Two organizations Zemo et al. 2017; CRC CARE 2017 have developed recommended toxicity factors to be applied to the polar metabolites. Although the fundamental approach used in both cases is the same, the specific assumptions used differ, resulting in the development of different toxicity factors for the polar metabolites. In both cases, assumptions were made about the composition of the metabolite mixtures in various stages of weathering of the released product and toxicity factors were assigned to the assumed compositions. The toxicity factors developed by CRC CARE 2017 were lower than those developed by Zemo et al. 2017; and the toxicity factors developed by both groups were lower that the toxicity factors that would be assigned if the polar fractions were assumed to consist of hydrocarbons. CRC CARE 2017 noted that while the toxicity assigned to the polar compounds is less that than that of the corresponding hydrocarbons, it is not so low that it can be disregarded.

Noteworthy assumptions associated with the evaluation of the toxicity mixtures of polar metabolites include the fact that the mixture will vary as a result of the source of the hydrocarbons, as well as the conditions and duration of weathering. Consequently, there would be uncertainty surrounding the chemical composition of the mixture in addition to the validity of the toxicity assigned to any fraction of metabolites. These uncertainties apply whether the toxicity factors specific to polar metabolites are used or whether the polar fractions are assumed to have the same toxicity as the corresponding hydrocarbons.

6.11 Toxicity Considerations for Different Exposure Routes

Any uptake of hydrocarbons into plant or animal material will also involve a substantial fractionation of the hydrocarbon mixture with only a subset of the hydrocarbons being absorbed into the plant or animal and distributed to the edible portions. As noted above, TPH extraction methods will extract chemicals other than hydrocarbon from plant and animal material. Accordingly, TPH analyses cannot be used for the evaluation of hydrocarbon exposure from consumption of plant and animal material. An indicator chemical approach is required instead.

Consideration of the site-specific hydrocarbon mixture to which plants and animals are exposed and the mechanism by which they may take up the hydrocarbons will be important in the selection of appropriate indicator chemicals. For plant and animal exposures involving migration or solution into water as a first step, one would need to consider the fact that hydrocarbons soluble in water would be expected to be limited primarily to aromatic compounds with carbon sizes of approximately C14 and lower, and that larger aromatic structures and almost all but the smallest aliphatic structures have limited solubilities in water.

As with hydrocarbons, different portions of the degradation product mixture can be expected to partition to different environmental media, based on their chemical and physical properties. When evaluating exposure via inhalation (e.g., from vapor intrusion), the chemical constituents expected are generally limited to the most volatile constituents of a released petroleum mixture. The mixture may include degradation products (e.g., methane), but is not likely to include polar metabolites. Selecting a hydrocarbon representative of the volatile hydrocarbons expected in indoor air and soil gas could address the toxicity of the parent hydrocarbons, as well as any degradation products for the inhalation exposure pathway.

When considering potential exposure from water, gasoline range compounds are thought to be essentially limited to soluble hydrocarbons and not to include polar metabolites, which are expected to have retention times that would be detected in the middle distillate range of a TPH analysis. TPH measured in water originating from releases of middle distillate products (e.g., diesel fuel, Stoddard solvent, heating oil, jet fuel, etc.) into water can be present in water largely, if not entirely, in the

form of polar degradation products. This is a function of the polar chemical structures, which are inherently more soluble in water than hydrocarbons. Hydrocarbons soluble in water from these products would be expected to be limited primarily to aromatic compounds with carbon sizes of approximately C14 and lower. Larger aromatic structures and almost all but the smallest aliphatic structures have limited solubilities in water.

Although it has been shown that polar degradation products can form in soil Mao et al. 2009a, general assumptions about the mix of metabolites and the fraction of material detected as TPH that is parent hydrocarbon versus metabolites are particularly elusive. Several factors that can affect the composition of polar degradation products following a petroleum release were identified (e.g., specific hydrocarbon product(s) released, chemical and microbial conditions in soil, time since release(s), etc.). It was also noted that a significant fraction of the material detected as TPH in soil samples analyzed by routine TPH analytical methods can be natural organic components of soil, particularly for organic-rich soil types, such as peat. The presence of such natural, organic soil components complicates any attempt to separately characterize the petroleum metabolites and parent petroleum compounds from the mixture of substances making up the TPH measured in soil samples.

It is plausible that TPH degradation products could be taken up in the food pathway as a result of irrigating food crops with water containing petroleum or as a result of uptake into fish from surface water releases, for example. It is not clear, however, which mixtures of degradation products or which individual degradation products would be taken up into a food exposure pathway, and thus, it is not clear what toxicity factors would be representative of any polar degradation products taken up into plants or animals in the food chain. Because many of the naturally occurring organic compounds making up plant and animal materials would report as TPH when measured using routine (bulk) TPH analyses, these analyses would not provide a valid measurement of the level of petroleum hydrocarbons or polar degradation products in plant or animal food products. Food pathways are typically evaluated using indicator chemical approaches. At some time in the future, it may be possible to select site-specific indicator chemicals for polar degradation products, but this is not currently possible using the best available scientific methods.

6.12 Risk Characterization

Risk characterization is the final step of the human health risk assessment process, and it has been described as the bridge between risk assessment and risk management because it provides a basis for risk estimation and an understanding of the results and uncertainties that are inherent in each step of the evaluation. ITRC 2015 described key issues associated with risk characterization and organized these into topic areas of risk results, presentation of risk results; and uncertainty and bias. More information on risk characterization is also available on USEPA's Human Health Risk Assessment web page (USEPA 2017c Step 4, Risk Characterization).

Major assumptions, scientific judgments, and to the extent possible, estimates of the uncertainties embodied in the risk assessment are presented in the risk characterization. For risk assessments involving TPH, the understanding and description of uncertainty and bias can be even more challenging because TPH is often viewed as a "complex mixture" that is unique from other complex mixtures (e.g., Aroclors). The approach to characterizing the risks from TPH may not be entirely unique, although many assumptions associated with the measurement, fate and transport, toxicity, and risk estimation for TPH are unique and will vary depending on the specific approach being taken to TPH in any given risk assessment. Identification and discussion of how the TPH-specific uncertainties can influence results and conclusions is an important component of any TPH risk assessments.