HUMAN HEALTH RISK ASSESSMENT (HHRA) NOTE 12
Guidance for Evaluating Human Health Risk at Sites Contaminated by Petroleum Hydrocarbons and Related Chemicals of Potential Concern (COPC)

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HUMAN AND ECOLOGICAL RISK OFFICE (HERO)

ISSUE DATE: June 2021

Summary**:**
This Human Health Risk Assessment (HHRA) note addresses the characterization and evaluation of the potential risks and hazards at sites contaminated with petroleum hydrocarbons, and other chemicals that are often associated with releases of petroleum and petroleum hydrocarbon-containing products. It is intended to supplement—not replace— other existing DTSC guidance documents, including but not limited to the Preliminary Endangerment Assessment (PEA) Guidance Manual (Cal/EPA, 2015a) and the Vapor Intrusion Guidance (DTSC, 2011). It is not intended to limit investigations at sites with a history of other hazardous material uses and does not diminish the need to collect additional samples to address on-site and off-site releases of hazardous substance other than petroleum and petroleum-related chemicals. It is not intended for certain fuel releases that fall under the Low-Threat Underground Storage Tank Case Closure Policy in California (SWRCB, 2012b). There might be other procedures that are technically equivalent, and we encourage discussion of any alternative approaches or methodologies under consideration in advance with the HERO toxicologist assigned to the site.

A quantitative risk evaluation of petroleum-contaminated sites should include the entire mixture quantified as Total Petroleum Hydrocarbons (TPH) in addition to the risk characterization for individually identified chemicals of potential concern (COPCs), such as specific volatile organic compounds (VOCs) for example benzene, semi volatile organic compounds (SVOCs) including polycyclic aromatic hydrocarbons (PAHs), and possibly metals. These individual COPCs should be assessed quantitatively using their specific toxicity criteria for both cancer risks and non-cancer hazards, as appropriate.

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1.0 Introduction

Releases of petroleum and petroleum products into the environment may include a wide variety of chemicals of potential concern (COPC). Some COPCs have been well studied and toxicologically characterized, such as benzene, toluene, ethylbenzene, xylenes, and polynuclear aromatic hydrocarbons (PAHs). However, most of the chemicals that constitute the mass of a petroleum spill, often referred to as total petroleum hydrocarbons (TPH), are not well understood and are difficult to evaluate. Nevertheless, all petroleum constituents should be evaluated for their impact on the environment and their potential toxic effects to human and ecological receptors (Ecological exposures are not covered in this document).

Although the term "TPH" is used often when discussing petroleum sites, this term is somewhat ambiguous. Rather than accurately representing all the hydrocarbons and their exact proportions in a release or oil spill, the term TPH is defined by the analytical method used to measure it (ITRC, 2018). There are several analytical methods for TPH and they all differ from each other in some respects. Many of the methods currently used by analytical laboratories involve solvent extraction followed by gas chromatography and flame ionization detection (FID). Because oils and petroleum products are complex mixtures of hundreds or thousands of hydrocarbons, the resulting chromatograms are not well resolved.

Some of the more common petroleum chemicals are benzene, butadiene, ethylbenzene, toluene, xylenes, hexane, naphthalene, benzo(a)pyrene, benzo(a)anthracene, and dibenzo(a,h)anthracene. However, these constituents make up only a small fraction of the petroleum mix and most petroleum releases are complex mixtures of thousands of chemicals. The petroleum composition depends on many factors, such as origin (crude oil type), intended use (automobile fuel, heating oil, lubricant, dry cleaning fluid or waste oil) and degree of weathering. Mixtures evaluated as TPH include crude oils, refined petroleum products (gasoline, diesel, and other fuels, lubricating and hydraulic oils, and solvents), waste oils, and process streams from refineries and other petroleum-related facilities.

For the purposes of this guidance, ITRC's 2018 definition of TPH will be used which is "the known or assumed aliphatic or aromatic hydrocarbon mixture (e.g., crude oil, fuel type, mixture of fuel types) originally released to the environment, or the remaining aliphatic and aromatic hydrocarbon mixture after weathering thereof, for the light non-aqueous phase liquid (LNAPL) in soil, and sediment sample matrices, and the dissolved hydrocarbons that have partitioned from the hydrocarbon mixture into groundwater or surface water for the water matrix, and the volatilized hydrocarbons that have partitioned from the hydrocarbon mixture or the dissolved phase to the soil vapor for the air matrix."

Reported TPH concentrations are often derived from a single, only partially resolved chromatogram. Laboratories may also divide the chromatogram into portions that roughly correspond to three common fuels or products that cover the range of most hydrocarbon contaminants expected at a site. For risk assessments, TPH has often been grouped into three hydrocarbon ranges according to the number of carbons and their functional uses: $TPH_{gasoline\ (TPHg)}$, $TPH_{diesel\ (TPHd)}$, and $TPH_{motor\ oil/residual\ range\ (TPHmo/rr)}$. Each of these ranges may then be further divided into aromatic and aliphatic fractions. TPH has also been grouped by some agencies into a weighted TPH composition (fuel type composed of various TPH fractions). For instance, instead of evaluating gasoline as a range of fractions (e.g., C5-C8 aliphatics, and C6-C8 aromatics) it is assumed to consist of a mixture with various percentages of C5-C8 and C9-C18 with the toxicity values applied proportionally resulting in a single weighted value (SFRWQCB, 2019). More infrequently, TPH may be reported in small incremental hydrocarbon ranges, such as C_5-C_6, C_7-C_8, etc. which can be combined to form the functional uses mentioned above. In addition to TPH, certain individual hydrocarbon constituents that are well characterized toxicologically (such as benzene) should be evaluated individually. These can be subtracted from the TPH measurements as described in Section 4.0.

The evaluation of potential risks and hazards associated with exposure to TPH presents many challenges. First, only a very small portion of the chemicals in TPH have been tested for toxicity individually. Furthermore, once released into the environment, even those petroleum products with known toxicity factors are likely to be subjected to weathering and therefore the resulting mixture will have a different composition compared to what was tested in toxicity studies. Moreover, a lack of sufficient toxicity information for petroleum mixtures presents additional challenges for risk assessments at sites that have multiple petroleum products or wastes.

Chemistry –

Petroleum mixtures such as crude oil or fuels consist of hundreds or thousands of different hydrocarbons that may be aliphatic or aromatic compounds which can vary in size from one to more than 100 carbon atoms. The smallest hydrocarbon is methane which consists of a single carbon atom surrounded by four hydrogen atoms, and is a gas at ambient temperatures and pressures, whereas larger hydrocarbons are liquid or solid under the same temperatures and pressures. Aliphatics may be straight-chained, branched, or cyclic molecules. Examples are hexane, isobutane or cyclopentane. Aromatic hydrocarbons, such as benzene, contain symmetrical ring structures. Some also contain aliphatic portions such as ethylbenzene. The rings are sometimes shown as having alternating single and double bonds. However, aromatic hydrocarbons have unique properties that result from the pi electrons being delocalized rather than fixed between two atoms on either end of a double bond. Only hydrocarbons with 4n+2 pi electrons, with n being an integer, can be aromatic. Aromaticity confers very different physical properties which affects fate and transport in the environment. Aromaticity also makes a hydrocarbon more reactive which can result in a different spectrum of biological and toxicological properties. Both aromatic and aliphatic compounds can be saturated or unsaturated. Unsaturated aliphatic hydrocarbons include those with double (alkenes or olefins) or triple (alkynes) bonds.

For additional information on petroleum refining, the physical and chemical properties, and environmental fate of petroleum, see the TPH Fundamentals chapter of ITRC's 2018 guidance on TPH Risk Evaluation at Petroleum Contaminated Sites.

Factors determining the environmental fate of hydrocarbons –
The composition of petroleum mixtures changes after their release into the environment because individual hydrocarbons differ in chemical and physical properties which leads to individual differences in the distribution between the non-aqueous phase liquid (NAPL) of the original release and the soil, water and vapor phases that form in all environments. The physical properties of a constituent depend on size, overall structure, and electron distribution in each type of hydrocarbon. For instance, smaller hydrocarbons with fewer carbon atoms are more likely to partition into vapor than large hydrocarbons. Large aliphatic hydrocarbons associate preferentially with other nonpolar hydrocarbons in the NAPL phase. Aromatics are more polar than aliphatic compounds due to their electron configuration and therefore more water soluble.

Understanding these properties is important because they govern the fate and transport as well as the composition of hydrocarbon mixtures in a given environmental medium. This can affect uncertainties of risk estimates and ultimately site management decisions. In general, the following can be said of the different hydrocarbon ranges.

- For the same number of carbons, aromatics are generally more water soluble than aliphatics.
- As the carbon number increases the hydrocarbon becomes less soluble.
- As the carbon number increases the hydrocarbon becomes less volatile.
- The more water soluble a COPC is the less likely it will volatilize from water. Partial degradation reduces both the effective solubility (solubility of a hydrocarbon from a NAPL mixture in water) and volatility of the remaining hydrocarbon mixture.

Weathering and Biodegradation –
After their release into the environment, petroleum mixtures change as the result of weathering. The most common weathering processes include volatilization (evaporation), dissolution into water, adsorption onto soil, and biodegradation. Some hydrocarbons may also be affected by photo-oxidation. The extent to which a particular hydrocarbon is affected by a given weathering process depends on its physical and chemical properties and the surrounding environment (e.g., climate, pH and redox potential of the soil, and soil bacterial content).

Most hydrocarbons are subject to biodegradation by many microorganisms which occurs as a series of oxidation steps. There are fundamental differences in the microbial processes involved in the degradation of aliphatic and aromatic hydrocarbons. Furthermore, the efficiency of degradation depends on site conditions as well as the structure of a hydrocarbon. Because biodegradation of each hydrocarbon involves many chemical reactions and frequently multiple types of microorganism, the observed final breakdown product is not always carbon dioxide (CO_2). In addition to microorganisms, which enable catalytic activities by providing enzymes, each hydrocarbon molecule requires a large number of oxygen molecules for “mineralization” or complete degradation (oxidation) to CO_2 or carbonate. This large amount of oxygen required (O_2 or other terminal electron acceptors) for complete degradation may not be readily available inside large hydrocarbon plumes.

Partial degradation products are most commonly observed in aqueous media such as groundwater. This is in part because biodegradation requires water and in part because the partial biodegradation products contain oxygen which makes them significantly more polar than the parent hydrocarbons and, hence, less biodegradable. These more polar products, which typically include multiple functional groups such as –OH (alcohol), =O (aldehyde or ketone), – COOH (acid), and – COOR (ester), have sometimes been called “polars”. Other names include “metabolites” which indicates that that they are products of microbial metabolism. However, some oxygen-containing partial degradation products are generated by photooxidation. Thus, the term “hydrocarbon oxidation products” or HOPs has recently been introduced for this group of petroleum-related contaminants.

2.0 Sampling Locations and Frequency

The following sampling suggestions may be applied to suspected release areas, or other areas needing sampling, such as exposure areas or decision units (DUs), hazardous and non-hazardous waste management units (HWMUs), operable units (OUs), or areas of concern (AOCs). More complex sites may require expanded sampling protocols. As with all site investigations, a conceptual site model (CSM) should be developed prior to sampling and updated as more information becomes available. It is recommended to include the initial CSM as part of a work plan prior to actual sampling. Information on the development of a CSM can be found in USEPA (1996), DTSC (2008a), or ITRC (2018). A CSM will help define the scope of the investigation and determine appropriate COPCs for the site, and the number, location, and frequency of sampling.

2.1 Sampling Overview

Sampling density, the number of samples for a certain area, may vary depending on property size, past operations, potential future land uses, and uncertainty of site conditions. Areas around abandoned petroleum production wells, fuel or oil storage tanks, waste storage and disposal areas, sumps, or surface drainages should be targets of focused sampling. Areas of discolored soil or stressed vegetation should also be sampled. In areas where historical information on site operations is unknown or insufficient, a random sampling or systematic grid-sampling program should be used in conjunction with results from soil gas surveys. Incremental Sampling Methodology (ISM) may also be used to evaluate exposure point concentrations (EPCs) for individual decision units (ITRC, 2020). Soil sampling should be extensive enough to determine the nature and extent of contamination and provide an estimate of the representative concentration of each COPC for each exposure area. Analyzing for TPH and/or individual COPCs is important for delineation (see Section 3 for discussion of analytical methods). Reporting different TPH fractions can be helpful depending on what type of petroleum product(s) were likely released at or near a given site, although analyzing for bulk TPH (i.e., non-fractionated TPHg, TPHd, TPHmo) may be sufficient at sites with minimal contamination. The use of volatile TPH, VOCs and some of the more volatile SVOCs at a site may require soil gas sampling in addition to soil sampling.

Analyses for non-petroleum hydrocarbon COPCs should be considered if they are known or suspected to have been used on-site. Dioxins, PCBs, PAHs, SVOCs, metals, chlorinated VOCs, and other COPCs should be considered if their use is suspected or the source of waste oil at the site is not known. Gasoline additives such as Methyl tertiary-Butyl Ether (MtBE), ethylene dichloride, ethylene dibromide, and tetraethyl lead may need to be considered depending on the age of the release[1].

2.1.1 Surface Soil

For human health risk assessments evaluations, surface soil is generally considered to be soil from ground surface to six inches below grade. When sampling surface soils for petroleum contamination, TPH, metals, and PAHs should be considered for inclusion in the list of analytes, although this may vary depending on the site's history. If waste oil is a contaminant then the analyte list could be extensive and be more than just used oil (e.g., dioxins, PCBs, etc).

Collecting surface soil samples for suspected spills of gasoline or other highly volatile mixtures may not be useful, due to evaporation, unless high concentrations are suspected, the contamination was recent, or if one is sampling immediately beneath building foundations or pavement. High contaminant concentrations may occur when petroleum fluids were released in large amounts directly to the ground, such as in waste pits, oil-water separators, floor drains, sumps and discharge pipes.

2.1.2 Subsurface Soil

The collection of subsurface soil samples is recommended at least every five feet during drilling. Soil samples should be visually inspected for signs of contamination such as discoloration, and samples should be screened with a field instrument such as a photoionization detector (PID). The results of the field screening should be recorded on the boring logs along with the occurrence of odors. Soil samples submitted for laboratory analysis should be selected from the field screening results. The number of samples for laboratory analysis should be dictated by the site's Data Quality Objectives (DQOs). Typically, samples with high contaminant concentrations as determined by field screening, odors, or visual staining should be subject to laboratory analysis. Staining associated with petroleum contamination often has a greenish hue but may also be brown or black. During drilling, boreholes should terminate in clean soil and a sample at depth should be collected to demonstrate vertical plume delineation. Soil sampling should continue until contaminant plumes are vertically and laterally

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[1] Tetraethyl lead (TEL) is likely not present as TEL unless NAPL is present. In the absence of NAPL it is more likely present as inorganic lead

delineated. If on-site lithologic information is not available prior to conducting the field investigation, one or more boreholes should be cored continuously.

Soil sampling strategies should also rely on selecting sample depths based on lithology characteristics and potential migration pathways. To characterize VOCs adequately in the vadose zone, a sampling strategy should focus on sampling fine-grained intervals and suspected or known contaminated soil horizons. For petroleum-release sites, the Sampling and Analysis Plan (SAP) should specify that fine-grained intervals will be analyzed for VOCs, PAHs, and metals. Analysis for additional COPCs may be warranted if they are believed to have been used or spilled on site. If VOCs are encountered or suspected, a follow-up soil gas survey should be conducted.

2.2 Soil Sample Collection for VOCs

In general, sites with VOCs, including gasoline and diesel range hydrocarbons should be characterized using both soil gas and soil samples. Soil samples are used to evaluate exposure via skin absorption, inhalation of particles, ingestion exposure pathways, and leaching potential of COPCs to groundwater; soil gas samples are used to evaluate vapor intrusion into structures.

Soil samples for VOC analysis should be collected and prepared in accordance with USEPA Method 5035. See DTSC (2004) for more information on Method 5035 sampling. Sample collection should be performed to minimize volatilization and biodegradation of VOC contaminants (e.g., methanol preservation or airtight samplers may be used). Samples collected in brass or stainless-steel sleeves should be subcored immediately upon removal from the sampling tool to minimize contaminant volatilization, and then must be preserved, as soon as possible. The sample collection method and preservation method should be documented in the chain of custody. Soil samples should not be collected in large bottles, wide-mouthed jars, or acetate liners. These are not appropriate containers under Method 5035 and are not appropriate sample collection devices for risk assessment purposes.

2.3 Background Metals

Metals contamination can be associated with petroleum release sites. For site metals characterization, an evaluation should be made to determine if site metal concentrations exceed natural background conditions. Further guidance on background sampling and the associated analysis can be found in DTSC (2008a).

2.4 Water

Surface water and/or groundwater can be affected by petroleum leaks or spills. Whenever there is a potential for petroleum to reach groundwater or surface water, an assessment should be conducted to evaluate potential impacts to water quality as well as potential migration of contamination and possible exposure of human and/or ecological receptors. When sampling surface water or groundwater, analytes to be considered in addition to TPH should include VOCs, fuel oxygenates, metals, and PAHs depending on the CSM. As mentioned in Section 1, the polar metabolites or HOPs which are generated through partial biodegradation of hydrocarbons are relatively water-soluble (in contrast to the parent hydrocarbons) and partition preferentially into the aqueous phase where they can reach concentrations that are orders of magnitude higher than those of parent hydrocarbons. Information about the presence or absence of HOPs should be documented and included in the CSM (See Section 3.3 on Silica Gel Cleanup). Procedures for the installation of groundwater monitoring wells and protocols for the acquisition of groundwater samples that are representative of aquifer conditions can be found in DTSC (2014), DTSC (2008b) and USEPA (2002). Water samples should be free of soil particles which may contain adsorbed hydrocarbons so that the analysis result accurately reflects the dissolved hydrocarbons. If NAPL is present in monitoring wells, this should be documented for remediation purposes.

2.5 Soil Gas

Soil gas sampling should be considered when the presence of volatile petroleum constituents or other VOCs are known or suspected (for example large and/or recent gasoline releases). Initial sampling should occur in the area of suspected contamination and continue until any soil gas plumes have been delineated. For general guidance on collecting multiple lines of evidence for vapor intrusion investigations please refer to DTSC's VI Guidance (DTSC, 2011), for soil gas sampling see the soil gas advisory (CalEPA 2015b).

Soil gas sample locations should be decided on a site-specific basis and designed taking into consideration the CSM, historical site use, known or potential release sources as well as other factors that affect soil gas migration, such as presence of buildings, soil type, and presence of preferential pathways. Initial spacing can be grid-based such as samples spaced on a 50- by 50-foot grid if source areas are unknown. Alternatively, initial sampling can be based on historical or suspected site use. When areas of contamination are identified, a more focused grid spacing, or biased sampling approach may be employed. Use a close interval grid or radial or step-out sampling pattern such as 10- to 20-foot grid pattern. Vertical soil gas delineation is needed as well, using multi-level sampling at 5-, 10-, 15-feet below ground surface down to non-detect or the capillary fringe to vertically delineate identified contaminant areas. If historical information for the area is unknown, a screening grid pattern, such as 100- by 100-foot may be used. Vertical soil gas sampling should be conducted to determine the source depth of subsurface contamination.

Sorbent tubes, passivated Summa cannisters, and glass or stainless steel airtight vials can be used to sample for volatile TPH. Contact DTSC should you wish to use a different container.

When evaluating vapor intrusion, sampling soil gas immediately adjacent to a building's foundation may be a viable option if the samples are collected near the contaminant source. Soil gas samples collected immediately above the source of contamination are more likely to be representative of what may be in contact with the building's foundation (Hers et al., 2006 and DiGiulio and Cody, 2006). The numerical modeling conducted by Abreu and Johnson (2005) and Abreu and others (2006) also suggests this relationship. Accordingly, collecting soil gas samples near contaminant sources is recommended by USEPA and DTSC for vapor intrusion modeling.

In general, soil gas samples should be collected as described by Cal-EPA (2015b). The vapor intrusion investigation of petroleum constituents should be conducted in accordance with DTSC (2011) and SWRCB (2012a). These documents may undergo revision; therefore, the most current version should be used. Additional information regarding the analysis of soil gas samples for TPH can be found in Section 3.2 below.

Some chemicals used for leak detection (e.g., isopropyl alcohol or isobutane) may cause false positives and increased reporting limits if present at greater than 0.01% due to significant dilutions performed by the lab. Helium may be used instead but is not without its issues including the need to have the lab run a separate analysis to determine if present (ITRC, 2014, 2018).

3.0 Analytical Methods

This section provides an overview of the methods that meet data quality objectives (DQOs) for environmental investigations of petroleum contaminated sites. Appendix A, Table A.1 **Recommended Analytical Methods for Target Analytes and Total Petroleum Hydrocarbon (TPH) Fractions for Petroleum Products** is intended as a guide to methods for analyzing environmental media for petroleum constituents at hydrocarbon release sites. Project managers and field personnel should be familiar with these analytical methods prior to field activities. Additional details on analytical methods can be found in ITRC's TPH Risk Evaluation guidance (ITRC, 2018).

Since it would not be practical to evaluate every hydrocarbon in petroleum-contaminated media, several approaches were developed to assess the bulk of a release as fractions grouped together based on fate and transport properties or toxicological properties, as advocated by the TPH Criteria Working Group (TPHCWG) and the Massachusetts Department for Environmental Quality (see below). To generate carbon fractions, hydrocarbons are extracted and separated by gas chromatography. Silica gel, a reagent that separates chemicals based on polarity, is sometimes used for generating separate aliphatic and aromatic fractions. At other times, silica gel is used to separate the polar hydrocarbon oxidation products from the parent hydrocarbons (see section 3.4).

For many sites with petroleum contamination where the data will be used for human health risk assessment, DTSC recommends the use of analytical methods that provide fractionation data for TPH, to provide aromatic and aliphatic hydrocarbon ranges for TPHg, TPHd, and TPHmo. However, TPH fractionation data may not be needed at sites with minimal contamination. Consequently, since the decision as to whether to use fractionation data or bulk TPH data depends on site-specific conditions, it is important to make sure that all relevant DTSC technical support staff review the work plans in advance of any site work to determine if the approach proposed is acceptable to achieve the DQOs for risk assessment and all other intended uses of the data. At many sites individual petroleum hydrocarbons such as benzene, toluene, ethylbenzene, etc. will also be evaluated individually.

3.1 Soil

Analyses for gasoline, diesel and motor oil hydrocarbons in soil samples can be performed using several methods depending on whether data for specific COPCs, bulk TPH, or fractionated TPH data are needed.

Bulk TPH data may be used to determine the nature and extent of petroleum contamination. Additional samples can be collected for fractionated TPH analysis for risk assessment purposes, if needed for a more accurate assessment. Table A1 (Recommended Analytical methods for Target Analytes and Total Petroleum Hydrocarbon (TPH) Fractions for Petroleum Products and Wastes) of this guidance provides recommendations for analysis for both bulk and fractionated hydrocarbon data. If only bulk data are needed then HERO recommends methods based on USEPA Method 8015B/C/D, or 8260B/C (GRO).

If a more robust, risk assessment of petroleum contamination is needed it should be based on fractions (i.e., fractionation) of aromatic and aliphatic compounds where the petroleum is classified according to carbon range. If fractionated data are needed for soil, then we recommend the use of the Massachusetts Department of Environmental Protection Volatile Petroleum Hydrocarbons/Extractable Petroleum Hydrocarbons (MADEP VPH/EPH) methods. However, other acceptable methods than those in Table A1 are available and should be fully explained and justified in the sampling workplan.

In the absence of fractionated analytical data, and/or when additional sampling is not feasible, the potential health risk associated with exposure to TPH in soil can be evaluated using a default fraction for the carbon range of aromatic or aliphatic compounds of 50% aliphatics and 50% aromatics (See Section 4.0 for additional information).

For analyses of the individual constituents of petroleum such as VOCs, SVOCs, PAHs, metals, and other COPCs, use USEPA SW-846, Clean Water Act, or equivalent analytical methods. See Table A1 (Recommended Analytical methods for Target Analytes and Total Petroleum Hydrocarbon (TPH) Fractions for Petroleum Products and Wastes) of this guidance for more specific information on methods.

In general, the analytical methods mentioned in this guidance cannot quantify metabolites or HOPs. In addition, there is a limit as to how large a hydrocarbon chain can be analyzed by the methods in Table A1. Hence, some of the hydrocarbons are unaccounted for in a risk evaluation, which adds to the uncertainty of the risk estimates.

3.2 Water

As with soil, several laboratory methods for TPH in water samples are available (see Table A1). HERO recommends the same methods for testing groundwater samples as are recommended for testing soil samples to obtain both fractionated and bulk TPH data as well as individual constituent data. Fresh releases of refined petroleum products that have not undergone significant weathering are expected to have a limited solubility in water. Moreover, as mentioned in Section 1, larger hydrocarbons are less soluble than small ones, aliphatic hydrocarbons are less soluble than aromatics and biodegradation increases solubility because it forms oxygen-containing metabolites or HOPs.

When evaluating the potential for adverse human health effects from petroleum in water the primary interest is in those hydrocarbon fractions that dissolve in water. By definition, NAPL is a separate phase and is not soluble in water. Petroleum hydrocarbon mixtures are usually light NAPLs. NAPL floating on groundwater may result in spurious analytical results if not removed prior to collecting water samples. Typically, the decision to remove NAPL does not require a risk assessment.

Note that due to low water solubility, the motor oil range of hydrocarbons (≥C16) is not likely to be found dissolved in significant concentrations. However, samples should be collected and analyzed, and the chromatogram evaluated to verify this. It is likely that the predominant compounds will be HOPs. Note also, that the presence of non-dissolved hydrocarbons may result in interference of the dissolved hydrocarbon analysis.

For risk assessment purposes, unfractionated groundwater TPH-g data should be assumed to be comprised of 100% aromatic compounds unless/until additional data become available.

3.3 Soil Gas

Table A-1 provides methods for the evaluation of TPH and its constituents. For risk assessment evaluation of TPH in soil gas or air HERO recommends the use of the MADEP Air-Phase (MADEP-APH) method (MADEP, 2009; SWRCB 2012a)[2]. USEPA Method 8015, as modified for air analysis, can be used for TPHg and TPHd bulk analysis but we recommend against its use for all but screening risk assessments due to the lack of fractionation. If different methods are preferred, then the DTSC project toxicologist should be consulted.

For individual volatile petroleum constituents (e.g., BTEX, PAHs and other COPCs) USEPA Method 8260, as modified for air analysis, TO-15, or TO-17 can be used for the determination of individual petroleum constituent concentrations.

For heavier petroleum hydrocarbons, such as those in the diesel range or higher, a combination of TO-15 (cannister sample collection) and TO-17 (adsorbent tube sample collection) may be needed. TO-15 may only detect hydrocarbons up to C10 (aromatics) and C12 (aliphatics), leaving some of the heavier (C12-C16), yet still volatile, hydrocarbons unaccounted for in a risk assessment. TO-17 can be used to evaluate

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[2] This is not the same as the MADEP-VPH method, which can be used for volatile TPH fractions in soil or water

hydrocarbons constituents heavier than C10. However, as of Summer 2021 there is no established USEPA method for fractionating these higher hydrocarbon ranges using thermal desorption with GC/MS methods. This has resulted in some laboratories developing their own methods which can lead to uncertainty in the concentration term. Until more data are collected, DTSC recommends that the decision as to whether air-phase fractionated data are needed for diesel range hydrocarbons be made on a site-specific basis in consultation with the toxicologist assigned to the site.

In the absence of fractionated data for soil gas or air, DTSC recommends that a ratio for petroleum of 75% aliphatics to 25% aromatics be used for risk assessment purposes.

For the analysis of hydrogen sulfide and other reduced sulfur chemicals, DTSC recommends using USEPA Method 16 or South Coast Air Quality Management District (SCAQMD) Method 307-91. Methane should be evaluated using USEPA Method TO-3, USEPA Method 3C, or modified USEPA Method 8015C calibrated with methane. A methane-specific field detector (e.g., LANDTEC GA-90, GEM-500, GEM-2000, or equivalent) may be used but DTSC should be contacted regarding its suitability.

3.4 Silica Gel Cleanup

Silica gel cleanup (SGC) methods such as USEPA Method 3630C are used to separate more polar from less polar chemicals. Method 3630 is sometimes used for “cleaning up” water samples prior to extractable bulk TPH or DRO/TPHd analysis with USEPA Method 8015. This treatment removes polar compounds, the bulk of which are mostly partial petroleum breakdown products or HOPs from the remaining non-polar parent hydrocarbons. This results in a TPH concentration that reflects the amount of parent hydrocarbons only. During investigations of petroleum contaminated sites SGC is primarily used for water samples but can also be applied to soil extracts. It was originally intended for sites with a high background of biogenic chemicals, which are present due to decaying vegetation. However, biogenic interference is not a common problem and the potential for that should be apparent from the CSM in which case samples collected downgradient of the release can be compared to samples collected from a similar setting immediately upgradient to help determine whether biogenic sources are responsible or something else such as degradation of petroleum. The use of SGC causes the polar HOPs to be excluded from the risk assessment, yielding estimates that will under predict the risk from exposure to the petroleum mixtures. Information about the identity and toxicity of the polar compounds is sparse making risk characterization difficult. If the TPH is evaluated without SGC, HOPs, metabolites, and the parent hydrocarbons are included in the result, and the reported analytical results may not strictly reflect petroleum hydrocarbons. DTSC recommends inspecting chromatograms for typical TPH patterns to help distinguish TPH from HOPS. Fact Sheet A.5 of the ITRC TPH Risk Evaluation guidance (ITRC, 2018) may be useful in evaluating chromatograms.

See next paragraph and Section 4.0 for additional information on how to use the results of SGC in a risk assessment.

For risk assessments at sites with relatively minor petroleum contamination, Method 8015 can be used without SGC to provide a screening risk assessment of the potential hazard of TPH. If the results indicate a potentially significant hazard index, then a more robust risk assessment can be performed by using hydrocarbon fractions. In either case, the qualitative evaluation of TPH results from Method 8015 both with and without SGC can be valuable in some circumstances when evaluating petroleum and its degradation byproducts. This information can be used as another line of evidence to indicate whether a TPH groundwater plume is biodegrading.

Additional information about Silica Gel Cleanup can be found in Fact Sheet A3 of the ITRC TPH Risk Evaluation guidance (ITRC, 2018).

4.0 Risk Assessment

This Human Health Risk Assessment (HHRA) guidance focuses on the aspects of risk assessment that are either not common to other chemicals or are not addressed in other DTSC guidance documents. See DTSC's Human and Ecological Risk Office's website for a listing of available guidance documents.

The evaluation of petroleum contaminated sites should include characterization of the TPH contamination and the potential health risk associated with it, as well as with the individual petroleum constituents that may be associated with the petroleum release, such as BTEX, PAHs, metals, and other contaminants as mentioned previously.

Evaluation of individual petroleum constituents (e.g. benzene, ethylbenzene, toluene, PAHs), along with the TPH fractions, may result in an over-estimation of petroleum-related hazard. Therefore, the concentrations of the individual COPCs that are evaluated separately in the risk assessment can be subtracted from the appropriate TPH fraction if both are being evaluated for non-cancer hazard. Note that this should only be done if both the individual and TPH fraction analysis were performed using the same analytical method and preferably by the same laboratory. The laboratory may be able to perform this separation if asked.

If the site is relatively simple and the extent of the contamination is limited, then a screening risk assessment can be performed. If the site is more complex, or a more precise risk assessment is needed, then a more robust assessment of TPH should be performed. See below for more information.

Screening Level Assessment

A screening level assessment of TPH would generally consist of data from Method 8015 B/C/D analyses (GRO, DRO and MO), without SGC, and the use of a default assumption of the ratio between aromatics and aliphatics. Other screening, or more robust, assessments may be acceptable, and HERO recommends discussing the preferred approach with the DTSC toxicologist for the site to determine whether a screening assessment is appropriate. Screening level assessments can be used for those sites where the TPH data are several years old and additional sampling and analysis are not planned or needed, or for newer, smaller sites with minimal contamination.

The screening assessment may consist of a simple quantitative risk evaluation performed using algorithms from USEPA's RAGS for the appropriate exposure pathways, based on the CSM, or from comparing maximum concentrations for the various media and COPCs with screening levels such as DTSC's Human Health Risk Note 3 (DTSC 2020).

Although HHRA Note 10 does not contain toxicity values for TPH, it has the following statement regarding choosing toxicity values for screening or cleanup values. "Until OEHHA or USEPA IRIS issues final toxicity criteria for TPH mixtures, DTSC will continue its long-standing practice of using toxicity criteria for TPH fractions that are consistent with HSC §25356.1.5(c)". Further information on this can be found in Section 4.2 below.

More Detailed Risk Assessment

A more robust risk assessment would generally involve the use of detailed TPH analysis.

Detailed analyses allow for a more specific quantification of petroleum hydrocarbons in various media and provides the aliphatic and aromatic concentrations so that a default value does not have to be used. The result is a more accurate estimate of risk, but the laboratory analysis costs are increased. Thus, hydrocarbon fractionation may not be useful on smaller or less complex sites where a screening assessment may be sufficient.

4.1 Exposure Assessment

Different constituents of petroleum contamination can partition into soil, water and air, and can also be found as a separate phase (e.g., NAPL) in the environment. Depending on the analytical results from the different media, all of the common exposure routes such as direct exposure, ingestion and inhalation should be considered, at least initially. The exposure routes can be changed based on the CSM. Petroleum mixtures can encompass a large range of physical properties among its constituents (e.g., highly volatile to relatively non-volatile). For risk assessment purposes, the potential for vapor intrusion from TPH may be one pathway of potential concern when buildings are near or over contamination.

To evaluate the vapor intrusion pathway in a risk assessment, DTSC recommends a multiple lines of evidence approach using the data collected following the recommendations in Section 3.3, as well as DTSC's Vapor Intrusion Guidance (DTSC 2011), and other guidance that is released after this petroleum evaluation guidance has been published. To estimate the human health risk of vapor intrusion from soil gas into indoor air one may use an attenuation factor to estimate indoor air concentrations. As of the publication of this guidance (i.e., Winter 2021) version 6.0 of USEPA's Johnson & Ettinger model is not recommended due in part to unspecified errors in it.

DTSC may consider the limited use of vapor intrusion models that account for aerobic biodegradation as another line of evidence in their decision making. However, this may require additional data including but not limited to results from soil gas analysis for O_2, CO_2, and CH_4. Contact the DTSC project toxicologist for further details.

For a more detailed discussion and review of petroleum vapor intrusion (PVI) and PVI models the ITRC Petroleum Vapor Intrusion guidance document (ITRC 2014) is a good resource. USEPA's Petroleum Vapor Intrusion Guidance (USEPA, 2015) is another resource.

4.2 Toxicity Criteria

Toxicity values for individual COPCs should come from DTSC's HHRA Note 10 (DTSC, 2019) in order to be in compliance with California's Toxicity Criteria Rule. The State of California Office of Administrative Law approved Title 22, California Code of Regulations Section 69021, *Toxicity Criteria for Human Health Risk Assessments, Screening Levels, and Remediation Goals* (Toxicity Criteria rule) on September 4, 2018. The rule adopts specific Office of Environmental Health Hazard Assessment (OEHHA) toxicity criteria listed in Appendix I of the rule and requires their use in human health risk assessments, human health risk-based screening levels and human health risk-based remediation goals (cleanup levels) (https://dtsc.ca.gov/regs/toxicity-criteria-for-human-health-risk-assessment). Toxicity values and screening levels that adhere to this rule can be found in DTSC's HHRA Note 10 (https://dtsc.ca.gov/wp-content/uploads/sites/31/2019/02/HHRA-Note-10-2019-02-25.pdf), and HHRA Note 3 (https://dtsc.ca.gov/wp-content/uploads/sites/31/2019/04/HHRA-Note-3-June-2020-A.pdf).

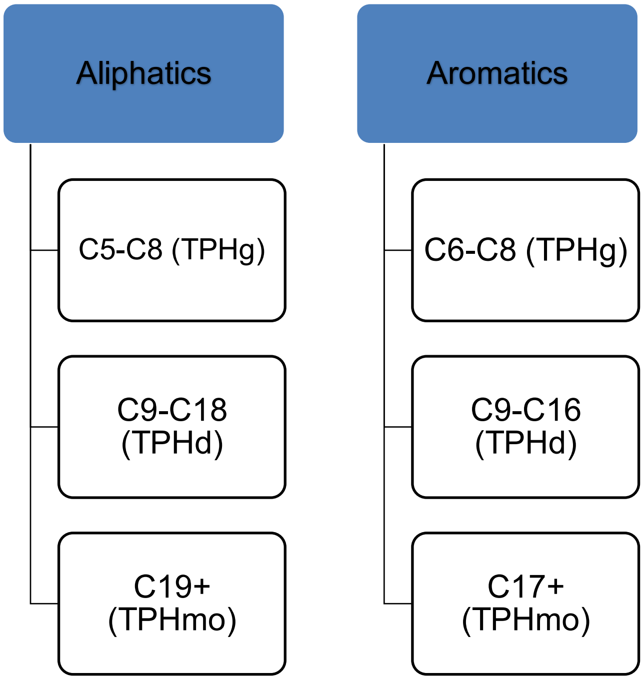
Toxicity values for TPH carbon ranges have not been developed by OEHHA and are not present in USEPA's IRIS database. However, according to DTSC's HHRA Note 10 "the selection of TPH toxicity criteria to use in a human health risk assessment and risk-based decision making depends on the specific analytical method(s) and TPH fraction definition used to analyze the contaminated media at the site. Selection of the appropriate toxicity criteria will depend on these factors and will necessarily be site-specific" There are several sources of toxicity values for TPH mixtures including the USEPA Provisional Peer-Reviewed Toxicity Values (PPRTVs) (USEPA, 2009), Massachusetts Department of Environmental Protection (MADEP, 2003), and Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG, 1997a).

Another option for evaluating TPH is to use the toxicity values in Table 4.2 that were developed for fractionated hydrocarbons. These were developed by HERO from existing toxicity values developed by other agencies and supplemented by information from studies found in publicly available literature. Information on how each value was determined can be found in Appendix B.

TPH is often divided into six fractions by carbon range and molecular structure (aliphatic vs. aromatic) for risk assessment or fate and transport purposes (See example below).

This approach was used by MADEP (2003) which developed their ranges with a focus on toxicity. The TPHCWG followed by developing 13 fractions with a focus on environmental fate and transport (TPHCWG 1997). The six fractions below were chosen with a focus on toxicity, rather than fate and transport, so that they could be evaluated in a risk assessment using the available analytical methods.

Figure 1. Aliphatic and Aromatics Hydrocarbon Fractions: The six representative, well-studied hydrocarbon or defined mixture fractions that have been recommended by HERO as chemical surrogates for toxicity (see Table 4.2**).**



For those sites where the TPH analytical data do not correspond exactly with the fractions listed above the DTSC toxicologist should be contacted to determine which toxicity values should be used for the fraction. DTSC acknowledges that that there are sites with TPH data, especially for older sites, that do not correspond exactly to the fractions above or to toxicity fraction data used by other regulatory agencies. DTSC is available to assist in these evaluations.

As per Sections 3.1 through 3.3, in the absence of aromatic vs. aliphatic speciation data, HERO recommends using a default assumption of 50% aromatics and 50% aliphatics as a health protective assumption for soil, and 100% aromatics for water, and 75% aliphatics and 25% aromatics for soil gas and air. For sites which may contain heavy oils, aromatic oils, or specialty chemicals derived from petroleum, this assumption may not be applicable and site-specific speciation data should be collected. Site-specific fractionation is recommended for sites with a significant amount of petroleum contamination as this will improve the accuracy of the risk assessment.

Toxicity criteria for potential carcinogenic effects of TPH mixtures are not available. Therefore, carcinogenic risk at sites with TPH should be evaluated by using cancer slope factors for individual carcinogens (e.g., benzene, ethylbenzene, polynuclear aromatic hydrocarbons, MtBE) when these chemicals are present. In addition to TPH all COPCs suspected or known to be present should also be evaluated in the risk assessment.

Table 4.2
TPH Toxicity Criteria[1]

Exposure Route	Carbon Range	RfD (mg/kg/day)
Oral	Aliphatic	
Oral	C_5-C_8	**0.04**
Oral	C_9-C_{18}	**0.1**
Oral	C_{19+}	**2.0**
Oral	Aromatic	
Oral	C_6-C_8	**Evaluate each COPC (e.g. BTEX)**
Oral	C_9-C_{16}	**0.004/0.03**#
Oral	C_{17+}	**0.03**

Exposure Route	Carbon Range	RfC (mg/m^3)
Inhalation	Aliphatic	
Inhalation	C_5-C_8	**0.7**
Inhalation	C_9-C_{18}@	**0.2**
Inhalation	C_{19+}	*
Inhalation	Aromatic	
Inhalation	C_6-C_8	**Evaluate each COPC (e.g., BTEX)**
Inhalation	C_9-C_{16}@	**0.05**
Inhalation	C_{17+}	*

\# 0.03 mg/kg-day may be used instead of 0.004 mg/kg-day if naphthalenes and methylnaphthalenes have been analyzed and evaluated individually.

@ It is likely that gasoline and diesel will be in the range of C_5-C_{12}.

* Not developed due to low volatility of the COPCs in this hydrocarbon range. Although inhalation exposure to C_{17+} TPH may occur via TPH bound to airborne dust. HERO does not recommend performing a quantitative evaluation of inhalation exposure for C_{17+} because of the significant uncertainty due to a lack of toxicity studies for inhalation of C_{17+} hydrocarbons.

[1] Toxicity criteria are based on USEPA's IRIS, 2021, MADEP, 2003, and TPHCWG, 1997. See Appendix B for details.

4.2.1 Toxicity of partial breakdown products (HOPs or metabolites)

The quantitative evaluation of weathered-petroleum mixtures containing HOPs is more difficult than that of fresh petroleum mixtures with lower concentrations of HOPs. Thus, for the most part, the toxicity of HOPs at petroleum contaminated sites has been ignored or the partial biodegradation products have been removed from water samples using silica gel cleanup (SGC). SGC primarily addresses middle distillate range products such as diesel fuel in water, because one cannot use SGC on volatile compounds such as gasoline, and the motor oil range hydrocarbons are not water soluble. One could evaluate the extent of HOPs formation in soil by comparing duplicate samples analyzed with and without SGC pretreatment but this is not commonly done in environmental investigations because the polar HOPs partition preferentially into water. As mentioned previously, analytical methods evaluating HOPs are not addressed in this document and are not in common use at most commercial laboratories that analyze environmental samples. Hence, the metabolites in a TPH sample are not typically identified nor quantified but are included in the fraction analysis when not using SGC. Without identifying the metabolite, it's risk cannot be calculated. Additionally, many HOPs have been identified but toxicity data are lacking.

As noted in ITRC's TPH Risk Evaluation at Petroleum Contaminated Sites guidance (ITRC, 2018) there are at least two options for addressing HOPs quantitatively in environmental investigations. One is to assume that they have the same toxicity as their parent hydrocarbon compound, the other is to use toxicity values of surrogates for the HOPs.

For the first option the toxicity values applied to TPH data from weathered petroleum spills are based on toxicity criteria that were developed for parent hydrocarbons, and not their various metabolites. Whether the toxicity of the bulk parent hydrocarbons is similar to the toxicity of more complex partially degraded petroleum mixtures containing metabolites is unsettled and may continue to change over time (ITRC, 2018). The second option is to assign toxicity values based on surrogates to metabolite families such as alcohols, acids, ketones and others. However, there is uncertainty in these values because they assume a certain composition of the mixtures, which may not be indicative of site-specific conditions.

Based on the issues raised above DTSC is not recommending quantitative evaluations of metabolites for all sites although an evaluation may become necessary at sites where petroleum releases threaten water resources. In the interim, these issues should be addressed in the uncertainty section of a risk assessment.

4.3 Risk Characterization, Cumulative Risk and Uncertainties

To the extent that numerical values are available for cancer risk and non-cancer hazard of individual compounds and mixtures associated with a petroleum-contaminated site, the individual, and cumulative risk and hazard should be calculated, and all site related chemical releases (for example metals, chlorinated solvents or pesticides) should be included with the petroleum associated hazard and risk values. Because petroleum releases are typically complex mixtures that pose challenges for analysis and risk evaluation a section on the uncertainties should be provided.

A final note: We recommend that petroleum hydrocarbon ranges not be segregated by target organ due to significant uncertainty about which target organs could be affected.

This type of segregation consists of segregating the hazard index by target organ and is typically performed when the total hazard index is found to be greater than 1.

The issue is not the use of surrogates for toxicity values, which has its own inherent uncertainty, but instead treating the surrogates as though they represent the entirety of the toxicity for a particular hydrocarbon range. There is too much uncertainty to make decisions involving distinguishing toxicity differences among different carbon ranges. In general, the use of surrogates to represent petroleum hydrocarbon ranges means that only a small subset of the chemicals present is assessed for toxicity.

REFERENCES

Abreu, L. D., and P. C. Johnson, 2005. Effect of Vapor Source - Building Separation and Building Construction on Soil Vapor Intrusion as Studied with a Three-Dimensional Numerical Model. Environmental Science and Technology, v. 39, no. 12, p. 4550 - 4561.

Abreu, L., P. Johnson, and T. McAlary, 2006. *3D Model Simulations and Implications to Near Building Sampling.* In the Proceedings of the Air and Waste Management Association Vapor Intrusion Work Shop, San Diego, California; March 16, 2006.

Cal/EPA, 2015a. State of California, Environmental Protection Agency. Department of Toxic Substances Control. *Preliminary Endangerment Assessment Guidance Manual.* Interim Final, October. (https://dtsc.ca.gov/wp-content/uploads/sites/31/2018/01/PEA_Guidance_Manual.pdf)

Cal/EPA. 2015b. Regional Water Quality Control Board, Los Angeles Region and Department of Toxic Substances Control. *Advisory – Active Soil Gas Investigation*. July. (https://dtsc.ca.gov/wp-content/uploads/sites/31/2018/01/VI_ActiveSoilGasAdvisory_FINAL.pdf)

DiGiulio, D., and R. Cody, 2006. Evaluation of the "Constrained Version" of the J&E Model and Comparison of Soil-Gas and Sub-Slab Air Concentrations at the Raymark Superfund Site. AEHS Vapor Intrusion Work Shop, San Diego, California; March.

DTSC, 2004. Department of Toxic Substances Control. Guidance Document for the Implementation of United States Environmental Protection Agency Method 5035: Methodologies for Collection, Preservation, Storage, and Preparation of Soils to be Analyzed for Volatile Organic Compounds. November. (https://dtsc.ca.gov/wp-content/uploads/sites/31/2016/01/HWMP_Guidance_Method-5035.pdf)

DTSC, 2008a. Department of Toxic Substances Control. *Proven Technologies and Remedies Guidance; Remediation of Metals in Soil*. August. (https://dtsc.ca.gov/wp-content/uploads/sites/31/2016/01/Guidance_Remediation-Soils.pdf)

DTSC. 2008b. Department of Toxic Substances Control. *Guidance Manual for Ground Water Investigations; Representative Sampling of Groundwater for Hazardous Substances*. February. (https://dtsc.ca.gov/wp-content/uploads/sites/31/2018/09/SMP_Representative_Sampling_GroundWater.pdf)

DTSC, 2011. Department of Toxic Substances Control. *Guidance for the Evaluation and Mitigation of Subsurface Vapor Intrusion to Indoor Air (Vapor Intrusion Guidance)*. October. (https://dtsc.ca.gov/wp-content/uploads/sites/31/2018/01/Final_VIG_Oct_2011.pdf)

DTSC, 2014. Department of Toxic Substances Control. *Well Design and Construction for Monitoring Groundwater at Contaminated Sites*. June. (https://dtsc.ca.gov/wp-content/uploads/sites/31/2018/09/Well_Design_Constr_for_Monitoring_GWContam_Sites1.pdf)

DTSC, 2020. Department of Toxic Substances Control. *Human Health Risk Assessment Note 3, DTSC Modified Screening Levels (DTSC-SLs).* June. (https://dtsc.ca.gov/wp-content/uploads/sites/31/2019/04/HHRA-Note-3-June-2020-A.pdf)

DTSC, 2019b. Department of Toxic Substances Control. *Human Health Risk Assessment Note 10, Toxicity Criteria*. February. https://dtsc.ca.gov/wp-content/uploads/sites/31/2019/02/HHRA-Note-10-2019-02-25.pdf

Hers, I., H. Dawson, and R. Truesdale, 2006. *Testing Exterior Tier 3 Screening with Site Data.* AEHS Vapor Intrusion Work Shop, San Diego, California; March.

ITRC (Interstate Technology & Regulatory Council). 2020. *Incremental Sampling Methodology Documents.* Washington, D.C.: Interstate Technology & Regulatory Council, Incremental Sampling Methodology Team (https://www.itrcweb.org/Guidance/ListDocuments?TopicID=11&SubTopicID=16)

ITRC (Interstate Technology & Regulatory Council). 2014. *Petroleum Vapor Intrusion, Fundamentals of Screening, Investigation and Management*. Washington, D.C.: Interstate Technology & Regulatory Council, Petroleum Vapor Intrusion Team. (https://www.itrcweb.org/PetroleumVI-Guidance/)

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

Johnson, P. C., and R. A. Ettinger, 1991. *Heuristic Model for Predicting the Intrusion of Contaminant Vapors into Buildings.* Environmental Science and Technology, v. 25, no. 8, p. 1445 – 1452.

MADEP, 2002. Commonwealth of Massachusetts, Department of Environmental Protection. Characterizing Risks Posed by Petroleum Contaminated Sites. October. (https://www.mass.gov/files/documents/2016/08/oj/02-411.pdf)

MADEP, 2003. Commonwealth of Massachusetts, Department of Environmental Protection. *Updated Petroleum Hydrocarbon Fraction Toxicity Values for the VPH/EPH/APH Methodology*. Final, November. (https://www.mass.gov/files/documents/2016/08/ok/tphtox03.pdf)

MADEP, 2009. Commonwealth of Massachusetts, Department of Environmental Protection. *Method for the Determination of Air-Phase Petroleum* Hydrocarbons *(APH).* Final, Revision 1.

(https://www.mass.gov/files/documents/2017/12/21/MassDEP%20APH%20Method%20-%20December%202009%20v1.pdf)

SFRWQCB, 2019. San Francisco Bay Regional Water Quality Control Board, Users Guide: Derivation and Application of Environmental Screening Levels (ESLs) INTERIM FINAL 2019 (Revision 1). (https://www.waterboards.ca.gov/sanfranciscobay/water_issues/programs/ESL/ESLs.html)

SWRCB, 2012a (Revised December 2015). State Water Resources Control Board. *Leaking Underground Fuel Tank Guidance Manual*. (https://www.waterboards.ca.gov/ust/luft_manual/manual_dec2015.pdf)

SWRCB, 2012b. *State Water Resources Control Board. Low-Threat Underground Storage Tank Closure Policy*. (https://www.waterboards.ca.gov/ust/lt_cls_plcy.html#policy081712)

TPHCWG, 1997. Total Petroleum Hydrocarbon Criteria Working Group. *Volume 3. Selection of Representative TPH Fractions Based on Fate and Transport Considerations.* Amherst Scientific Publishers, Amherst, MA. July.

TPHCWG, 1997a. Total Petroleum Hydrocarbon Criteria Working Group. Volume 4. Development of Fraction Specific Reference Doses (RfD) and Reference Concentrations (RfC) for Total Petroleum Hydrocarbons (TPH). Amherst Scientific Publishers, Amherst, MA.

USEPA, 1996. United States Environmental Protection Agency. *Attachment A, Conceptual Site Model Summary; Soil Screening Guidance: User's Guide (Second Edition)*. Document No. EPA 540/R-96/018. July. (https://hwbdocuments.env.nm.gov/Los%20Alamos%20National%20Labs/References/9702.PDF)

USEPA, 2002. United States Environmental Protection Agency. *Ground-Water Sampling Guidelines for Superfund and RCRA Project Managers: Ground Water Forum Issue Paper*. Office of Solid Waste and Emergency Response, Document No. 542/S-02/001. May (https://www.epa.gov/sites/production/files/2015-06/documents/gw_sampling_guide.pdf)

USEPA, 2009. United States Environmental Protection Agency. *Provisional Peer-Reviewed Toxicity Values for Complex Mixtures of Aliphatic and Aromatic Hydrocarbons (CASRN Various).* Superfund Health Risk Technical Support Center, Office of Research and Development (https://hhpprtv.ornl.gov/issue_papers/ComplexMixturesofAliphaticandAromaticHydrocarbons.pdf)

USEPA, 2015. United States Environmental Protection Agency. *Technical Guide for Addressing Petroleum Vapor Intrusion at Leaking Underground Storage Tank Sites*. EPA 510-R-15-001. (https://www.epa.gov/sites/production/files/2015-06/documents/pvi-guide-final-6-10-15.pdf)

USEPA, 2021. United States Environmental Protection Agency. *Integrated Risk Information System*. (https://www.epa.gov/iris)

Appendix A

Table A.1

Recommended Analytical Methods for Target Analytes and Total Petroleum Hydrocarbon (TPH) Fractions for Petroleum Products and Wastes. References for analytical methods in this table include the Environmental Chemistry Laboratory of the Department of Toxic Substances Control (Standard Operating Procedures), California State Water Resources Control Board (Leaking Underground Fuel Tank Guidance Manual 2012) (SWRCB, 2012a) and Massachusetts Department of Environment Protection (Policy #WSC-02-411 on Characterizing Risks Posed by Petroleum Contaminated Sites: Implementation of the MADEP VPH/EPH Approach) (MADEP, 2002, 2009).

Petroleum Product	Media	Target Analytes & Hydrocarbon Fraction	Filtering Step	Extraction Method(s)	Analytical Method(s)	Cleanup Method(s)
Gasoline (C4-C12)	Soil / Ground water	BTEX, naphthalene, MTBE, TBA, EDB, EDC	*Groundwater: Centrifuged, gravity-separated, or filtered with 0.7µm glass-fiber	Soil: EPA 5030 or 5035 Ground water: EPA 5030	EPA 8260B/C (GC/MS)	NA
Gasoline (C4-C12)	Soil / Ground water	BTEX, naphthalene, MTBE, TBA, EDB, EDC	*Groundwater: Centrifuged, gravity-separated, or filtered with 0.7µm glass-fiber	MADEP-VPH (GC/PID /FID)	MADEP-VPH (GC/PID/FID)	NA
Gasoline (C4-C12)	Soil / Ground water	C5-C8 Aliphatics	*Groundwater: Centrifuged, gravity-separated, or filtered with 0.7µm glass-fiber	MADEP-VPH (GC/PID /FID)	MADEP-VPH (GC/PID/FID)	NA
Gasoline (C4-C12)	Soil / Ground water	C9-C12 Aliphatics	*Groundwater: Centrifuged, gravity-separated, or filtered with 0.7µm glass-fiber	MADEP-VPH (GC/PID /FID)	MADEP-VPH (GC/PID/FID)	NA
Gasoline (C4-C12)	Soil / Ground water	C9-C10 Aromatics	*Groundwater: Centrifuged, gravity-separated, or filtered with 0.7µm glass-fiber	MADEP-VPH (GC/PID /FID)	MADEP-VPH (GC/PID/FID)	NA

Petroleum Product	Media	Target Analytes & Hydrocarbon Fraction	Filtering Step	Extraction Method(s)	Analytical Method(s)	Cleanup Method(s)
Gasoline (C4-C12)	Soil / Ground water	C5-C12 TPH	*Groundwater: Centrifuged, gravity-separated, or filtered with 0.7µm glass-fiber	Soil: EPA 5021, 5030 or 5035 Groundwater: EPA 5030	EPA 8015B/C/D (GC/FID)	NA
Gasoline (C4-C12)	Soil Vapor	BTEX, naphthalene, 1,3-butadiene, MTBE, EDB, EDC	NA	NA	Modified EPA 8260B/C, TO -15, or TO-17 (GC/MS)	NA
Gasoline (C4-C12)	Soil Vapor	BTEX, naphthalene, 1,3-butadiene, MTBE, EDB, EDC	NA	NA	MADEP-APH (GC/MS)	NA
Gasoline (C4-C12)	Soil Vapor	C4-C12 TPH	NA	NA	Modified EPA 8260B/C, TO -15, or TO - 17 (GC/MS)	NA
Gasoline (C4-C12)	Soil Vapor	C5-C8 Aliphatics	NA	NA	MADEP-APH (GC/MS)	NA
Gasoline (C4-C12)	Soil Vapor	C9-C10 Aromatics	NA	NA	MADEP-APH (GC/MS)	NA
Diesel Fuel / Middle Distillates (C8-C30)	Soil / Ground Water	BTEX, naphthalene, MTBE	*Groundwater: Centrifuged, gravity-separated, or filtered with 0.7µm glass-fiber	Soil: EPA 5030 or 5035 Groundwater: EPA 5030	EPA 8260B/C (GC/MS)	NA
Diesel Fuel / Middle Distillates (C8-C30)	Soil / Ground Water	BTEX, naphthalene, MTBE	*Groundwater: Centrifuged, gravity-separated, or filtered with 0.7µm glass-fiber	MADEP-VPH (GC/PID/FID)	MADEP-VPH (GC/PID/FID)	NA

Petroleum Product	Media	Target Analytes & Hydrocarbon Fraction	Filtering Step	Extraction Method(s)	Analytical Method(s)	Cleanup Method(s)
Diesel Fuel / Middle Distillates (C8-C30)	Soil	PAHs	NA	Soil: EPA 3540C, 3541, 3546 or 3550C	EPA 8270C/D SIM	No SGC. Polar metabolites, byproduct of biodegradation of petroleum hydrocarbon are present in extract. **EPA 3630C (SGC) Fractionation surrogates. Remove polar metabolites.
Diesel Fuel / Middle Distillates (C8-C30)	Ground water	PAHs	*Groundwater: Centrifuged, gravity-separated, or filtered with 0.7μm glass-fiber	Ground water: EPA 3510C or 3520C	EPA 8270C/D SIM	No SGC. Polar metabolites, byproduct of biodegradation of petroleum hydrocarbon are present in extract. **EPA 3630C (SGC) Fractionation surrogates. Remove polar metabolites.
Diesel Fuel / Middle Distillates (C8-C30)	Soil / Ground water	C9-C18 Aliphatics	*Groundwater: Centrifuged, gravity-separated, or filtered with 0.7μm glass-fiber	MADEP-EPH (GC/FID & GC/MS)	MADEP-EPH (GC/FID & GC/MS)	Fractionation surrogates. Elute w/ hexane.
Diesel Fuel / Middle Distillates (C8-C30)	Soil / Ground water	C19-C36 Aliphatics	*Groundwater: Centrifuged, gravity-separated, or filtered with 0.7μm glass-fiber	MADEP-EPH (GC/FID & GC/MS)	MADEP-EPH (GC/FID & GC/MS)	Fractionation surrogates. Elute w/ hexane.

Petroleum Product	Media	Target Analytes & Hydrocarbon Fraction	Filtering Step	Extraction Method(s)	Analytical Method(s)	Cleanup Method(s)
Diesel Fuel / Middle Distillates (C8-C30)	Soil / Ground water	C11-C22 Aromatics	*Groundwater: Centrifuged, gravity-separated, or filtered with 0.7µm glass-fiber	MADEP-EPH (GC/FID & GC/MS)	MADEP-EPH (GC/FID & GC/MS)	Fractionation surrogates. Elute w/ methylene chloride
Diesel Fuel / Middle Distillates (C8-C30)	Soil / Ground water	C12-C22 TPH Diesel	*Groundwater: Centrifuged, gravity-separated, or filtered with 0.7µm glass-fiber	Soil: EPA 3540C, 3541, 3546 or 3550C Ground water: EPA 3510C or 3520C	EPA 8015B/C/D (GC/FID)	No SGC. Polar metabolites, byproduct of biodegradation of petroleum hydrocarbon are present in extract. **EPA 3630C (SGC) Fractionation surrogates. Remove polar metabolites, byproduct of biodegradation of petroleum hydrocarbon
Diesel Fuel / Middle Distillates (C8 - C30)	Soil / Ground water	C23-C32 Motor Oil	*Groundwater: Centrifuged, gravity-separated, or filtered with 0.7µm glass-fiber	Soil: EPA 3540C, 3541, 3546 or 3550C Ground water: EPA 3510C or 3520C	EPA 8015B/C/D (GC/FID)	No SGC. Polar metabolites, byproduct of biodegradation of petroleum hydrocarbon are present in extract. **EPA 3630C (SGC) Fractionation surrogates. Remove polar metabolites, byproduct of biodegradation of petroleum hydrocarbon

Petroleum Product	Media	Target Analytes & Hydrocarbon Fraction	Filtering Step	Extraction Method(s)	Analytical Method(s)	Cleanup Method(s)
Lubricating & Hydraulic & Waste Oils (C25-C36)	Soil / Ground water	BTEX/VOCs, EDB, EDC, M TBE, TBA	*Groundwater: Centrifuged, gravity-separated, or filtered with 0.7µm glass-fiber	Soil: EPA 5030 or 5035 Groundwater: EPA 5030	EPA 8260B/C (GC/MS)	NA
Lubricating & Hydraulic & Waste Oils (C25-C36)	Soil / Ground water	PAHs	*Groundwater: Centrifuged, gravity-separated, or filtered with 0.7µm glass-fiber	Soil: EPA 3540C, 3541, 3546 or 3550C Ground water: EPA 3510C or 3520C	EPA 8270C/D SIM	No S G C. Polar metabolites are present in extract. **EPA 3630C (S G C) Fractionation surrogates. Remove polar metabolites, byproduct of biodegradation of petroleum hydrocarbon
Lubricating & Hydraulic & Waste Oils (C25-C36)	Soil / Ground water	Metals (Cd, Cr, Ni, Pb, Zn)	NA	Soil: EPA 3050B Groundwater: EPA 3010A	EPA 6010B/C (ICP/AES)	NA
Lubricating & Hydraulic & Waste Oils (C25-C36)	Soil / Ground water	C23-C34 TPH (Soil Only)	NA	Soil: EPA 3540C, 3541, 3546 or 3550C	EPA 8015B/C/D (GC/FID)	No S G C. Polar metabolites, byproduct of biodegradation of petroleum hydrocarbon are present in extract. **EPA 3630C (S G C) Fractionation surrogates. Remove polar metabolites, byproduct of biodegradation of petroleum hydrocarbon

Notes:
* Discussion and justification are needed for any filtering technique applied to groundwater samples.
** Use of EPA 3630C (Silica Gel Cleanup) for removal of polar metabolites from biodegradation of petroleum hydrocarbons must be fully documented and demonstrated to meet quality control requirements of method and overall project objectives.

Acronyms:

BTEX	Benzene, toluene, ethylbenzene and xylene
EDB	1,2-dibromoethane
EDC	1,2-dichloroethane
Metals	Cadmium, chromium, mercury, nickel, lead and zinc
MTBE	Methyl *tertiary* butyl ether
PAH	Polycyclic aromatic hydrocarbon = In this guidance the term "PAH" typically refers to the 16 USEPA priority PAHs naphthalene, acenaphthene, acenaphthylene, anthracene, phenanthrene, fluorene, chrysene, fluoranthene, pyrene, benzo(b)fluoranthene, benzo(a)pyrene, benzo(k)fluoranthene, benzo(a)anthracene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene
SGC	Silica gel cleanup
TBA	*tert*-Butyl alcohol
VOC	Volatile organic compound

Appendix B

Development of non-cancer toxicity criteria for TPH

B.1 C_5-C_8 (aliphatics)

The recommended non-cancer oral and inhalation toxicity reference values for evaluating exposure to aliphatic hydrocarbons in the C_5-C_8 range are 0.04 mg/kg-day, and 0.7 mg/m^3 (0.2 mg/kg-day) respectively. These toxicity criteria are based on toxicological studies of n-hexane, which is believed to be the most toxic constituent of the C_5-C_8 range of aliphatics. The oral toxicity value was derived by MADEP in their VPH/EPH/APH Methodology (MADEP, 2003). The inhalation toxicity value of 0.7 mg/m^3 is the DTSC and USEPA Reference Concentration (RfC) for n-hexane (USEPA, 2021, DTSC, 2019).

The critical study for the oral toxicity value, performed by Krasavage et, al. (reviewed in MADEP, 2003), was an evaluation of hexane given to rats orally at doses of 570, 1140, or 4000 mg/kg-day, 5 days per week for 90 to 120 days. The reference value is based on the lowest-observed-adverse-effect-level (LOAEL), of 570 mg/kg-day. The critical effects at the lowest does were decreased body weight gain, and nervous system changes at the higher doses.

The USEPA RfC for hexane is based on peripheral neuropathy observed in rats in a subchronic inhalation study. Studies of humans exposed occupationally to hexane by inhalation also showed peripheral neuropathy. However, the available occupational studies were confounded by co-exposure to other solvents, some of which may potentiate n-hexane induced toxicity.

DTSC/HERO is aware of studies showing that C_5-C_8 aliphatics other than n-hexane appear to cause neurotoxicity at doses higher than with n-hexane, and that there is evidence indicating that they may decrease the neurotoxicity of n-hexane in mixtures. Studies of di-ketone metabolites, reviewed in MADEP, 2003, indicated that the target organ of n-hexane may be the central nervous system, while being less toxic than other C_5-C_8 metabolites to peripheral nerves. However, the data are insufficient to derive separate toxicity values for the non-hexane hydrocarbons. Therefore, because these other hydrocarbons also cause neurotoxicity the reference value for n-hexane should be used until additional data are available.

B.2 C_6-C_8 (aromatics)

Aromatic hydrocarbons in the C_6-C_8 range, including benzene, toluene, ethylbenzene, and xylenes should be evaluated individually using toxicity values for each hydrocarbon.

B.3 C_9-C_{18} (aliphatics)

The recommended non-cancer oral and inhalation toxicity reference values for C_9-C_{18} aliphatic hydrocarbons are 0.1 mg/kg-day, and 0.2 mg/m^3 (0.09 mg/kg-day) respectively. The oral reference value is based on the results of several subchronic studies in rodents of various petroleum streams covering the aliphatic range of C_9–C_{17} (TPHCWG 1997). Change in liver weight was the most common critical effect in developing a toxicity criterion for each study. The reference value of 0.1 mg/kg-day for oral exposure is based on two studies with a no-observed-adverse-effect-level (NOAEL) of 100 mg/kg-day with an uncertainty factor of 1000, and a study with a LOAEL of 500 mg/kg/day and an uncertainty factor of 5000. Both TPHCWG (1997) and MADEP (2003) recommend this value for this hydrocarbon range.

The recommended value of 0.2 mg/m^3 is based on inhalation studies of petroleum streams within the C_9-C_{18} range evaluated by TPHCWG (1997) and by MADEP (2003) in their update of toxicity criteria for TPH. The LOAEL adjusted for continuous exposure, was approximately 1,000 mg/m^3 in developmental (gestational days 6-15, and subchronic (6 hours/day, 5 days/week for 12 weeks) studies of both C_{10}–C_{11} isoparaffinic hydrocarbons and C_7–C_{11} dearomatized white spirits in rats. The critical effects were changes in blood chemistry, and liver and body weight. MADEP applied an uncertainty factor of 3,000 for both studies. However, MADEP (2003) also evaluated four additional studies, including one of six-month duration and three of acute duration. MADEP used results from the six-month study of dearomatized white spirit in rats (Lund et al., 1995, as reviewed in MADEP, 2003) to develop an RfC of 0.2 mg/m^3 for the C_9-C_{18} aliphatic group. The study found changes consisting of later latency peaks of the flash evoked potential, somatosensory evoked potential, and auditory brain stem responses. There were no observed changes in learning and memory functions. The significance of the findings of the Lund et al. study for evaluation of neurotoxicity in humans was not clearly established.

B.4 C_9-C_{16} (aromatics)

The recommended non-cancer oral and inhalation toxicity reference values for aromatics of carbon number C_9-C_{16} are 0.004 mg/kg-day, and 0.05 mg/m^3 respectively. The reference value for oral exposure is based primarily on the USEPA oral RfD for 2-methylnaphthalene because methylnaphthalenes may comprise a significant portion of this hydrocarbon range. There are at least eight other aromatics in this hydrocarbon range for which RfDs have been derived (i.e., isopropylbenzene, naphthalene, pyrene, fluoranthene, fluorene, acenaphthene, anthracene, and biphenyl). The range of RfDs for all nine aromatics is 0.004 to 0.5 mg/kg-day ((DTSC, 2020; IRIS, 2021). Most of these have an oral RfD equal to or greater than 0.04 mg/kg-day. The only aromatics in this range with a lower RfD are naphthalene (0.02 mg/kg-day), and 2-methylnaphthalene (0.004 mg/kg-day). For sites at which naphthalene and the methylnaphthalenes are evaluated individually the MADEP RfD of 0.03 mg/kg-day can be used instead of 0.004 mg/kg.

The recommended toxicity criterion for evaluation of inhalation exposure is based on inhalation studies of C_9^+ aromatic mixtures. Both TPHCWG (1997) and MADEP (2003) based their respective RfCs on the same studies and critical effects (e.g., primarily body weight reduction, kidney and liver toxicity). The primary difference between the two was that MADEP used an extra uncertainty factor of 3 to account for the limited number of studies available. HERO agrees with this additional uncertainty factor and the resulting reference value of 0.05 mg/m^3. Please note that cancer risk and non-cancer hazard indices for speciated PAHs and other aromatics in this range should be calculated separately in addition to the evaluation for TPH.

B.5 C_{19+} (aliphatics)

The recommended non-cancer oral toxicity reference value for aliphatics of carbon number range C_{17+} is 2.0 mg/kg-day. This toxicity criterion is recommended by both TPHCWG (1997) and MADEP (2003). No toxicity reference value has been developed for inhalation. For the oral toxicity criterion both TPHWG and MADEP relied on a study of several white mineral oils conducted in 1996 by the British Industrial Biological Research Association (BIBRA). White mineral oils are mixtures of highly refined hydrocarbons consisting primarily of saturated paraffins (alkane hydrocarbons) and naphthenes (cycloalkanes) and have no aromatic constituents (TPHCWG 1997). Administration of several of the lower molecular weight white mineral oils resulted in liver granulomas, and histiocytosis in the mesenteric lymph nodes; higher MW white mineral oils had no adverse effect. The former was similar to findings in studies conducted by Baldwin, et. al (1992). The lack of significant toxicity of the white mineral oils of higher carbon number ($C_{>34}$, average MW of 480) has been attributed to lack of absorption of high molecular weight hydrocarbons (Albro and Fishbein, 1970 as cited in TPHCWG 1997). Based on these findings both TPHWG and MADEP recommend oral toxicity criteria of 2 mg/kg-day for C_{17} – C_{34} aliphatic hydrocarbons, and 20 mg/kg-day for >C_{34} aliphatic hydrocarbons. DTSC/HERO agrees with this evaluation and recommends using the toxicity criterion of 2 mg/kg-day to evaluate C_{19+} aliphatic hydrocarbons. Use of this value for C_{18+} hydrocarbons is a health protective approach.

An inhalation toxicity value has not been developed by TPHCWG (1997) or MADEP (2003) due to a lack of appropriate inhalation toxicity studies and because inhalation is not considered to be a significant exposure pathway for this TPH range. Hydrocarbons in this range have low volatility but might be found at very low concentrations in the vapor phase. Inhalation exposures to the vapor phase and to hydrocarbons bound to air-borne particulates can occur at TPH contaminated sites. However, DTSC/HERO agrees with TPHCWG and MADEP that the inhalation pathway is not expected to be a significant exposure pathway for this range of aliphatics. Furthermore, aliphatic hydrocarbons are generally less toxic than aromatics of similar hydrocarbon fractions (TPHCWG 1997).

B.6 C_{17+} (aromatics)

The non-cancer oral toxicity reference value for aromatics of carbon chain length C_{17+} is 0.03 mg/kg-day. No toxicity reference value has been developed for inhalation. Due to a lack of appropriate studies of this carbon range TPHCWG or MADEP selected a USEPA oral RfD for a surrogate to represent this group. Pyrene was chosen as the surrogate because it was the closest compound to this carbon length for which an RfD was available from the USEPA and DTSC’s HHRA Note 10. The oral RfD for pyrene is 0.03 mg/kg-day (DTSC, 2019; IRIS, 2021). Although there is a higher RfD for fluoranthene (C16; 0.04 mg/kg-day) DTSC/HERO agrees with TPHCWG and MADEP approach and has chosen 0.03 mg/kg-day to represent this TPH fraction.

An inhalation non-cancer toxicity value hasn't been developed for the C_{17+} aromatic fraction. No appropriate studies have been identified and, as with the similar fraction of aliphatic hydrocarbons, TPHCWG and MADEP do not consider inhalation to be a significant exposure pathway for this TPH range. DTSC/HERO agrees that inhalation exposures to vapor phase and/or particle-bound aromatic C_{17+} hydrocarbons are expected to be low relative to other exposure pathways. DTSC/HERO does not recommend performing a quantitative risk assessment for non-cancer effects for the inhalation pathway because of the significant uncertainty. Individual carcinogenic PAHs in this range will be evaluated for risks associated with all potential exposure pathways, including inhalation.

References

Baldwin, M.K., Berry, P.H., Esdaile, D.J., Linnette S.L., Martin, J.G., Peristianis, G.C., Priston, R.A., Simpson, B.J., & Smith, J.D. (1992). Feeding studies in rats with mineral hydrocarbon food grade white oils. Toxicol. Pathol., 20(3): 426-435.

DTSC, 2019. Department of Toxic Substances Control. *Human Health Risk Assessment Note 10, Toxicity Criteria*. February. (https://dtsc.ca.gov/wp-content/uploads/sites/31/2019/02/HHRA-Note-10-2019-02-25.pdf)

MADEP, 2003. Commonwealth of Massachusetts, Department of Environmental Protection. *Updated Petroleum Hydrocarbon Fraction Toxicity Values for the VPH/EPH/APH Methodology*. Final, November. (https://www.mass.gov/files/documents/2016/08/ok/tphtox03.pdf)

TPHCWG, 1997. Total Petroleum Hydrocarbon Criteria Working Group. Volume 4. Development of Fraction Specific Reference Doses (RfD) and Reference Concentrations (RfC) for Total Petroleum Hydrocarbons (TPH). Amherst Scientific Publishers, Amherst, MA.

USEPA, 2021. United States Environmental Protection Agency. *Integrated Risk Information System*. (https://www.epa.gov/iris)