Linda S. Adams
Secretary for
Environmental Protection

Department of Toxic Substances Control

Maziar Movassaghi
Acting Director
8800 Cal Center Drive
Sacramento, California 95826-3200

Arnold Schwarzenegger
Governor

Interim Guidance
Evaluating Human Health Risks from Total Petroleum Hydrocarbons (TPH)

Human and Ecological Risk Division
California Department of Toxic Substances Control
June 16, 2009

1.0 INTRODUCTION

The Department of Toxic Substances Control (DTSC) Human and Ecological Risk Division (HERD) has developed this guidance to address the characterization and risk evaluation of total petroleum hydrocarbons (TPH). This guidance is for use in analyzing and evaluating TPH data where some or all of the suspected contaminants are petroleum hydrocarbons. Additional chemicals of potential concern (COPC) that may also be present are also considered in this guidance.

This guidance is intended to supplement—not replace—DTSC guidance, including but not limited to the Preliminary Endangerment Assessment (PEA) Guidance Manual (Cal/EPA, 1999), the School Environmental Assessment Manual (DTSC, 2009), and other guidance related to DTSC programs. The guidance is not intended to limit investigations at sites with a history of other hazardous material uses and does not diminish the need to collect authoritative samples at additional site locations commonly associated with on-site and off-site hazardous substance releases. It provides a technical framework for evaluating TPH. Other technically equivalent procedures may exist, and this guidance is not intended to exclude alternate approaches or methodologies.

A quantitative risk evaluation of total petroleum hydrocarbons (TPH) should be performed regardless of its concentration at a site. This risk characterization should occur in addition to the risk characterization for individually identified TPH-related COPCs, such as benzene, polynuclear aromatic hydrocarbons (PAHs), and metals. These COPCs should be quantitatively assessed using their specific toxicity criteria for both cancer risks and non-cancer hazards, as appropriate.

Risk assessment for TPH presents a number of challenges. Out of the hundreds of chemicals in TPH only a very small portion have been tested for toxicity. Furthermore,

although some petroleum products, such as wholly vaporized unleaded gasoline, may have undergone toxicity testing, the product in the environment is likely to have undergone weathering and therefore is a different composition than what was originally tested. Therefore the results of the original testing may not be applicable for the weathered product. Moreover, sites that have multiple petroleum products or wastes, present additional considerations.

TPH may refer to a variety of products or wastes. However, for the purpose of risk assessments TPH is generally grouped into three ranges according to the number of carbon atoms: $TPH_{gasoline\ (g)}$, $TPH_{diesel\ (d)}$, and $TPH_{motor\ oil/residual\ range\ (mo/rr)}$. In some analyses, TPH may be reported in small incremental hydrocarbon ranges, such as C_5-C_6, C_7-C_8, etc., but generally, TPH is most often grouped into the three ranges mentioned above, plus total hydrocarbons.

2.0 TOTAL PETROLEUM HYDROCARBONS

Total petroleum hydrocarbons covers the wide range of chemicals composed of carbon and hydrogen that are found in crude oils, petroleum products (such as gasoline, diesel, and other fuels, lubricating and hydraulic oils, and solvents), wastes, and process streams from refineries and other petroleum-related facilities. The smallest and simplest petroleum hydrocarbon is methane and the largest is likely to be a hydrocarbon chemical containing greater than 34 carbon atoms. Some of the more well known petroleum hydrocarbons from a toxicological point of view include benzene, butadiene, ethylbenzene, toluene, xylenes, hexane, naphthalene, benzo(a)pyrene, benzo(a)anthracene, and dibenzo(a,h)anthracene.

TPH is usually present in the environment as a result of accidental spills, waste disposal, leaks from storage tanks, or other types of releases. It may also be found as a result of oil seepages from naturally occurring underground reservoirs of oil. Seeps may be found both offshore and onshore in California and tend to be found along the coast and in the San Joaquin Valley.

Concentrations of TPH in the environment may vary greatly, from low parts per million (ppm) in surface soils where gasoline has been spilled in small quantities to greater than 100,000 ppm in areas where crude oil has been stored or fuel leaks from pipelines or underground storage tanks have occurred.

TPH mixtures in the environment undergo a process called weathering in which natural processes such as volatilization or degradation occur, thereby changing the chemical composition of the original environmental contamination. During this process the lighter hydrocarbons (i.e., smaller molecular weight) decrease in concentration while relative concentrations of higher molecular weight (and carbon number) hydrocarbons in residual TPH increase. The longer the TPH remains in the environment and is subjected to weathering the less the TPH mixture resembles the product or waste that was originally spilled, leaked, or otherwise released.

3.0 SAMPLING LOCATIONS AND FREQUENCY

The following sampling suggestions may be applied to areas with suspected releases, or other defined areas needing sampling. The intent is to give a general outline of sampling protocols, with the knowledge that more complicated or diverse sites may require expanded sampling protocols. A conceptual site model (CSM) is recommended as part of a work plan prior to sampling. This will help narrow the focus of the investigation and help determine the COPCs to analyze for, and the number, location, and frequency of sampling.

3.1 Soil Matrix

Sampling frequency, the number of samples for a certain area, may vary depending on the size, past operations, and condition of the site. Areas around abandoned oil or gas wells, fuel or oil storage tanks, areas with visible contamination, waste storage and disposal areas, sumps, or surface drainages should be targets of focused sampling. Areas of discolored soil or where vegetation is stressed or non-existent should also be targets of focused sampling. In areas where past use or historical information is unknown or insufficient, a random sampling, or systematic grid-sampling program should be used in conjunction with results from soil gas surveys, in areas with suspected or known volatile TPH releases. Soil matrix sampling should be extensive enough to determine not only the nature of contamination but also its general extent. Analytes generally should include polynuclear aromatic hydrocarbons (PAHs) and total petroleum hydrocarbons (TPH) (see Section 4 for discussion of analytical methods). Evaluation of volatile organic compounds (VOC) may require soil sampling in addition to soil gas sampling at some sites (see Section 3.2).

Analyses for other chemicals of potential concern should be considered if they are known to have been used on-site. These may include CAM 17 metals, hexavalent chromium, SVOCs, and other site specific potential contaminants. There may also be circumstances where COPCs such as dioxins, PCBs, and/or other COPCs should be considered if the source of waste oil is not known.

3.1.1 Surface Soil

Surface samples (i.e., 0” to 6” below ground surface (bgs)) should be obtained for analysis of PAHs, metals, and TPH. Due to the high volatility of VOCs, analysis of surface soil samples for VOCs is not recommended unless there is reason to believe that high concentrations may be found or contamination was recent, or when sampling immediately beneath foundations or pavement. High concentrations may occur in waste pits, sumps, or in other areas where VOCs were disposed of or released or have been spilled in large amounts.

3.1.2 Subsurface Soil

Subsurface soil samples should be collected and obtained for the analyses of the chemicals evaluated in surface soils. In general, subsurface samples should be collected starting at 2.5 - 3.0 feet bgs and 5 feet bgs, and every 5 feet bgs thereafter until the extent of contamination is established. Other intervals may be required depending on site conditions, such as areas of known contamination or lithologic changes. A visual inspection of soil cores may be useful in providing an estimate of the extent of the heavier (i.e., oil, high carbon range compounds) petroleum contamination. However, the visual estimate should be confirmed by analytical data.

Soil sampling strategies should rely on selecting sample depths based on lithology, suspected contaminants, potential migration pathways, and field screening. To adequately characterize VOCs in the vadose zone, a sampling strategy should focus on sampling fine-grained intervals and suspected or known contaminated soil horizons (e.g., a black oily zone in a permeable sand layer). The sampling and analysis plan (SAP) should prescribe soil-sampling depths based on the most adsorptive or retentive lithology for each contaminant type. The SAP should specify that fine-grained intervals will be analyzed for VOC concentrations, if present, following a soil gas survey.

3.2 Soil Sample Collection for VOCs

In general, sites with VOCs should be characterized by soil gas samples; however, there may be sites where VOCs will need to be characterized in soil matrix samples, or both. Sites requiring soil matrix samples include those with high concentrations of TPH and/or co-contamination, sites with very fine-grained soils, and/or those with shallow ground water and capillary zone which preclude collecting and analyzing representative soil gas samples. Soil matrix samples for VOC analysis (if required) must be collected and prepared in accordance with USEPA Method 5035. See DTSC (2004a) for more information on Method 5035 sampling. The contractor should estimate the anticipated VOC concentrations in soil matrix and determine, with DTSC concurrence, the appropriate sampling and extraction procedure. Sample collection must be performed to minimize volatilization and biodegradation of VOC vapors. These samples collected in brass or stainless steel sleeves must be subcored immediately upon removal from the sampling tool to minimize the volatilization of chemicals of concern, appropriately preserved, and extracted as soon as possible. The sample collection and extraction times should be documented in the chain of custody. The use of an on-site mobile laboratory is recommended for larger sites in order to provide relatively rapid information. A subset of these samples should be sent to a fixed lab for confirmation.

3.3 Background Metals

The presence of metals in soil may be due to natural processes or may be from human activities. In general, it is DTSC's policy to evaluate quantitatively risk associated with metals present at concentrations above those of the naturally occurring background concentrations for the area of the site. A comparison of site concentrations of metals to area background concentrations for the area of the site can be made to determine which metals are likely present at elevated concentrations due to releases. To help

accomplish this soil samples should be collected from a minimum of four off-site locations not impacted by human activities and analyzed for CAM 17 metals. Other metals may also be evaluated for background as needed. Background concentrations of hexavalent chromium should be analyzed if it is found in site soil. These background locations should have soil with the same or similar properties to that of the site being investigated. Relevant data sets from previously obtained local background sampling can also be used if they can be shown to be applicable to the site being investigated. Soil samples from background locations should be analyzed for metals. Further guidance on background sampling can be found in *Selecting Inorganic Constituents as Chemicals of Potential Concern at Hazardous Waste Sites and Permitted Facilities* (DTSC, 1997), other guidance as appropriate, or by contacting DTSC.

3.4 Water

Sampling of water for TPH, and associated contaminants should follow the same general guidance as described above in Section 3.1 (Soil Matrix) with regard to what COPCs to look for. In addition, some of the oxygenates, such as MtBE, may be more of a concern in the site area than some of the other COPCs that are often found in the soil at a site.

Many site investigations do not need to include an investigation of groundwater, especially in the initial stage, because groundwater is too deep to have been contaminated by site contaminants, or because any releases were not significant in size. Therefore, the initial investigation may only involve soil and soil gas. If contamination is found to have occurred then a decision can be made with regard to the need for investigation of ground or surface water. In general, the use of a CSM can help with these decisions.

3.5 Soil Gas

Soil gas sampling should be considered for $TPH_{gasoline, and\ diesel}$, and VOCs with a Henry's Law constant of 1E-05 atm-m^3/mole or higher, or a vapor pressure of 1E-03 mmHg or higher. The soil must have adequate air permeability for soil gas samples to be collected. Initial sampling should occur in area of suspected contamination and should be obtained from 5 feet to evaluate potential shallow sources of contamination, and at 10 to15 feet bgs to evaluate potential deeper sources.

Samples should be collected near lithologic interfaces or based on field instrument readings (e.g., Flame Ionization Detector [FID], Photo Ionization Detector [PID]) from soil cuttings and/or cores to determine the location of maximum analyte concentrations. Use all available information (e.g., geologic log, organic vapor concentration reading) to select appropriate depths for vapor monitoring. Install probes at depths with elevated vapor readings and/or slightly above fine-grained soils. The deepest probe should be installed above the capillary fringe. Soil gas samples for VOC analysis should be collected in accordance with USEPA Method 5030 when analyzed using USEPA Methods 8015C, 8260B, and 8021B.

Deeper and/or additional sampling, such as subslab sampling beneath foundations, may be needed for some sites and the decision to do this may depend on the results of the initial sampling. The horizontal spacing for this initial sampling should be approximately 100 feet apart unless VOCs or other volatile gases of concern are known to be present, in which case sampling should occur every 20 feet.

Soil gas sampling and evaluation should be conducted in accordance with guidance found in *Advisory-Active Soil Gas Investigations* (DTSC and CRWQCBLAR, 2003), and *Interim Final- Guidance for the Evaluation and Mitigation of Subsurface Vapor Intrusion to Indoor Air* (DTSC, 2004b). Both of these documents are undergoing revisions, therefore the most current version should be used. Additional information regarding the analysis of soil gas samples for TPH can be found in Section 4.3 below.

4.0 ANALYTICAL METHODS

4.1 Soil Matrix

Although there are several methods available for the analyses of total petroleum hydrocarbons in soil, DTSC recommends analyses based on USEPA Method 8015C until such time as DTSC or Cal/EPA adopts or develops an analytical method(s) for TPH mixtures. Method 8015C allows for an approximate estimation of hydrocarbon ranges corresponding to what are commonly referred to as gasoline range organics (TPH_g), diesel range organics (TPH_d), and motor oil/residual range organics (TPH_{mo}).

The results of the TPH analyses can be used in assessing the nature and extent of contamination at a site, and as described in Section 5, for assessing potential human health risks associated with the contamination. Alternative analytical methods are available but DTSC should be contacted for approval prior to their use. For risk assessment purposes the fraction of aromatic and aliphatic compounds, and carbon range, should be provided as part of the analytical results. These fractions should be available from the laboratory conducting the TPH analysis. However, if these data are not available and additional sampling can't be conducted then the TPH ranges should be evaluated in the risk assessment using a default fraction for the carbon range of aromatic or aliphatic compounds. See Section 5.0.

For analyses of the individual components of petroleum, VOCs, PAHs, and metals, or other chemicals of potential concern (COPC) USEPA SW-846 or equivalent analytical methods should be used.

4.2 Water

As with the soil matrix sample analyses DTSC has not developed or adopted an analytical method(s) for TPH mixtures. Until such time as a method is officially adopted we recommend using USEPA Method 8015C, which allows for an approximation of hydrocarbon ranges corresponding to what are commonly referred to as gasoline range organics (TPH_g), diesel range organics (TPH_d), and motor oil/residual range organics

(TPH_{mo}). Other methods may be available but DTSC should be consulted prior to its use so that they may review the proposed methodology.

For analyses of the individual components of petroleum, VOCs, PAHs, and metals, or other chemicals of potential concern (COPC) USEPA SW-846, Clean Water Act, or equivalent analytical methods should be used.

4.3 Soil Gas

Analyses of volatile TPH gasoline and diesel fractions, and VOCs in soil gas samples can be performed using modifications of USEPA Methods 8015C, 8260B, and/or TO-15 depending on the detail needed. Other methods might be substituted in certain circumstances but the DTSC risk assessor should be consulted.

USEPA Method 8260B may be used for analysis of some of the VOCs associated with petroleum-contaminated sites and non-TPH co-contaminants. In addition, it can be used for determining total $TPH_{gasoline,}$ and may be able to be used for determining the aliphatic concentration. If risk-based detection limits or other DQOs cannot be met with USEPA Method 8260B for TPH and/or non-TPH contaminants, then samples should also be obtained using summa canisters and analyzed using USEPA Method TO-15 or equivalent.

On some sites there may be a need to determine aliphatics and aromatics more accurately. Some laboratories can determine this using an in-house method, or alternatively, they can be analyzed using the Massachusetts Department of Environmental Protection method (MADEP, 2008), which is based on TO-15. DTSC should review the proposed methodology prior to laboratory analysis.

Additional consideration is necessary for sites with potential contamination by naphthalene and methylnaphthalenes which are typically associated with diesel, jet fuels, weathered gasoline, and some solvent mixtures. These PAHs are sufficiently volatile and may be present in soil gas, posing potential inhalation risks. Soil gas sampling and analyses for naphthalene and 2-methylnaphthalene might require separate sampling and analysis by USEPA Method TO-17. However, soil matrix sampling and PAH analyses are also appropriate for these contaminants. DTSC should be consulted for development of the DQOs and site sampling and analysis plan for characterizing these constituents and associated risks.

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. The method used should allow for a method detection limit of 50 ppbv, or a detection limit of 500 ppbv. Methane should be evaluated using USEPA Method TO-3, USEPA Method 3C, or modified USEPA Method 8015C calibrated with methane. A methane-specific detector (e.g., LANDTEC GA-90, GEM-500, GEM-2000, or equivalent) may be used but DTSC should be contacted regarding its suitability. These detectors should have a lower detection limit for methane of at least 10,000 ppbv. Additional information can be found in guidance mentioned elsewhere in

this guidance as well as in DTSC's Advisory on Methane Assessment and Common Remedies at School Sites (http://www.dtsc.ca.gov/Schools/upload/SMBRP_SCHOOLS_Methane.pdf)

5.0 RISK ASSESSMENT

The risk assessment for TPH is the same in many respects as it is for other COPCs and therefore the details of each step of the risk assessment process will not be presented here except in those instances where it is not covered elsewhere. A quantitative risk evaluation of TPH should include characterization of the TPH contamination and the risk associated specific fractions, as well as with the individual components, such as BETX and PAHs.

DTSC risk assessment guidance can be found on the DTSC website at http://www.dtsc.ca.gov.

Many of the chemicals in TPH mixtures, as well as the hydrocarbon chain mixtures, have not been tested for toxicity. As a result TPH has often not been evaluated in risk assessments. To address the lack of chemical-specific criteria for many components of petroleum hydrocarbon mixtures, TPH can be generally evaluated through the use of surrogate chemicals. For risk assessments for sites with TPH contamination, DTSC/HERD recommends the use of the following six groups of hydrocarbons for which chemical surrogates for toxicity have been selected (see Section 5.2):

- C_5-C_8 (aliphatics)
- C_6-C_8 (aromatics)
- C_9-C_{18} (aliphatics)
- C_9-C_{16} (aromatics)
- C_{19+} (aliphatics)
- C_{17+} (aromatics)

These six groups and surrogates described below were chosen based in part on the TPH work performed by the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG, 1997-1999), and regulatory agencies such as the Massachusetts Department of Environmental Protection (MADEP, 2002 and 2003).

If the analytical method used during the site investigation did not provide speciation into aromatics and aliphatics then an assumption of a composition of 50% aromatics and 50% aliphatics can be made for most sites. Based on a review of the literature and data submitted to DTSC this generic composition split provides a health protective assumption without assuming that all of the detected hydrocarbons are aromatic. If the project proponent believes this too conservative an assumption for the site then additional analysis and/or sampling can be performed using analytical methods that do provide this speciation. For some sites, such as petroleum or chemical refineries, which

may contain heavy oils or aromatic oils, or specialty chemicals this assumption may not be applicable. In these cases a method that speciates TPH may be required.

5.1 Exposure Assessment

Because TPH mixtures can encompass of a large range of hydrocarbons, chemical properties and environmental behavior vary widely among components. Constituents of TPH range from highly volatile to relatively non-volatile. For risk assessment purposes, the potential for vapor intrusion into buildings from TPH components is of particular concern. TPH migration to groundwater is also a potential concern, but it is beyond the scope of this guidance.

Table 1 below contains some of the chemical properties that can be used for evaluating the potential for indoor vapor intrusion, using the Johnson & Ettinger model, from TPH for the C_5-C_8, and C_9-C_{18} fractions (TPHCWG, 1997a). The C_{17+} fraction(s) are assumed to be relatively non-volatile and non-mobile and are not included in the table.

Table 1
Chemical Properties of TPH

TPH	K_{oc}	D_a	D_w	S	H'	H	T_R	T_B	T_C	$\Delta H_{v,b}$
C_5-C_8 aliphatic	3981	0.1	1.0E-05	5.4	50	8.0E-01	25	369	508	7000
C_6-C_8 aromatic	251	0.1	1.0E-05	520	0.27	5.6E-03	25	383	617	8523
C_9-C_{18} aliphatic	251188	0.1	1.0E-05	0.034	120	1.9E+00	25	473	568.9	7000
C_9-C_{16} aromatic	2511	0.1	1.0E-05	25	0.14	1.2E-02	25	473	637	9321

K_{oc}- Organic partition coefficient (cm^3/g) (TPHCWG, 1997a, Table 8)
D_a- Diffusivity in air (cm^2/s) (TPHCWG, 1997a)
D_w- Diffusivity in water (cm^2/s) (TPHCWG, 1997a)
S- Solubility in water (mg/L) (TPHCWG, 1997a, Table 8)
H'- Henry's law constant (unitless) (TPHCWG, 1997, Table 8)
H- Henry's law constant at reference temperature ($atm\text{-}m^3/mol$)
T_R- Henry's law constant reference temperature (°C)
T_B- Normal boiling point (°K) (TPHCWG, 1997, Table 8)
T_C- Critical temperature (°K) (J&E Model, m-xylene, 135 trimethylbenzene)
$\Delta H_{v,b}$- Enthalpy of vaporization at the normal boiling point (cal/mol) (J&E Model, m-xylene, 135 trimethylbenzene)

5.2 Toxicity Criteria

Toxicity criteria for evaluating TPH mixtures in a risk assessment have not been developed by Cal/EPA Office of Environmental Health Hazard Assessment (OEHHA) or USEPA. Therefore DTSC/HERD has developed criteria for non-cancer health effects based in part on toxicity factors for noncancer health effects developed by TPHCWG

and MADEP (TPHCWG, 1997b; MADEP, 2003). Development of noncancer toxicity criteria for TPH groups is described in the subsections below and summarized in Table 2. 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, hexavalent chromium, etc.) 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.

5.2.1 C_5-C_8 (aliphatics)

The recommended non-cancer oral and inhalation toxicity reference values that should be used 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 component of the C_5-C_8 range of aliphatics. The oral toxicity value was derived by MADEP in the VPH/EPH/APH Methodology (MADEP, 2003). The inhalation toxicity value of 0.7 mg/m^3 is the USEPA Reference Concentration (RfC) for n-hexane.

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 were nervous system changes.

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/HERD is aware of studies showing that C_5-C_8 aliphatics other than n-hexane appears to cause neurotoxicity at higher doses than 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 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.

5.2.2 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.

5.2.3 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 0.3 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, 1997b). 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 an uncertainty factor of 1000, and a study with a LOAEL of 500 mg/kg/day and uncertainty factor of 5000. Both TPHCWG (1997b) and MADEP (2003) recommend this value for this hydrocarbon range.

The recommended value of 0.3 mg/m^3 is based on inhalation studies of petroleum streams within the C_9-C_{18} range evaluated by TPHCWG (1997b) and evaluated by MADEP (2003) in their update of toxicity criteria for TPH. The LOAEL adjusted for continuous exposure, was approximately 1,000 mg/m in 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. Therefore, DTSC/HERD recommends an RfC of 0.3 mg/m^3 as described above, rather than MADEP 2003 value of 0.2 mg/m^3.

5.2.4 C_9-C_{16} (aromatics)

The recommended non-cancer oral and inhalation toxicity reference values for unspeciated 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 the nine aromatics is 0.004 to 0.3 mg/kg-day. Most of these have an oral RfD of 0.04 mg/kg-day or higher. The only aromatics in this range with a lower RfD are pyrene (0.03 mg/kg-day), 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.

The recommended toxicity criterion for evaluation of inhalation exposure is based on inhalation studies of C_9 aromatic mixtures. Both TPHCWG (1997b) 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. HERD 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.

5.2.5 C_{18+} (aliphatics)

The recommended non-cancer oral toxicity reference value for aliphatics of carbon number range C_{18+} is 2.0 mg/kg-day. This toxicity criterion is recommended by both TPHCWG (1997b) 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 components (TPHCWG 1997b). Administration of several of the lower MW 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 1997b). 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/HERD agrees with this analysis and recommends using the toxicity criterion of 2 mg/kg-day to evaluate C_{18+} aliphatic hydrocarbons. Use of this value for C_{34+} hydrocarbons is a health protective approach.

An inhalation toxicity value has not been developed by TPHCWG (1997b) 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/HERD 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 1997b).

5.2.6 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. The oral RfD for pyrene is 0.03 mg/kg-day (IRIS, 2008). Although there is a higher RfD for fluroanthene (C16; 0.04 mg/kg-day) DTSC/HERD 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/HERD 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/HERD 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.

Table 2
TPH Toxicity Criteria

Exposure Route	Carbon Range	TPHCWG (mg/kg/day)	MADEP (mg/kg/day)	DTSC/HERD (mg/kg/day)	Critical Effect
Oral	**Aliphatic**				
	C_5-C_8	5	0.04	**0.04**	Neurotoxicity
	C_9-C_{18}	0.1	0.1	**0.1**	Change in liver weight
	C_{19}-C_{32}	2.0	2.0	**2.0**	Liver granuloma, histiocytosis in lymph nodes
	Aromatic				
	C_6-C_8	Evaluate benzene	Evaluate each COPC	**Evaluate each COPC (e.g. BTEX)**	Depends on COPC
	C_9-C_{16}	0.04	0.03^	**0.004/0.03#**	Lung, toxicity
	C_{17}-C_{32}	0.03	0.03^	**0.03**	Liver, kidney toxicity
		(mg/m^3)	**(mg/m^3)**	**(mg/m^3)**	
Inhalation	**Aliphatic**				
	C_5-C_8	18.4	0.2	**0.7**	Neurotoxicity
	C_9-C_{18}	1.0	0.2	**0.3**	Changes in blood chemistry, liver and body weight
	C_{19}-C_{32}	-*	-*		**-**
	Aromatic				
	C_6-C_8	Evaluate benzene	Evaluate each COPC	**Evaluate each COPC (e.g., BTEX)**	Depends on COPC
	C_9-C_{16}	0.2	0.05	**0.05**	Liver, kidney toxicity, body weight reduction
	C_{17}-C_{32}	-*	-*		-

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.
^ Value is for C9-C32
* 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 HERD does not recommend performing a quantitative evaluation of inhalation exposure for C_{17+} not be performed because of the significant uncertainty involved.

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