



STATE OF HAWAII
DEPARTMENT OF HEALTH
P. O. BOX 3378
HONOLULU, HI 96801-3378

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To: Kathleen S. Ho, JD
Deputy Director of Environmental Health

Through: Joanna L. Seto, PE, Chief
Environmental Management Division *Joanna L. Seto*

Gaudencio Lopez, PE, Chief
Safe Drinking Water Branch *Gaudencio C. Lopez*

Harold Lao, Acting Program Manager
Hazard Evaluation and Emergency Response Office *Harold Lao*

Diana Felton, MD, State Toxicologist
Hazard Evaluation and Emergency Response Office *Diana Felton*

From: Roger Brewer, PhD, Senior Environmental Scientist
Hazard Evaluation and Emergency Response Office *Roger Brewer*

Subject: Recommended Risk-Based Drinking Water Action Levels for Total Petroleum Hydrocarbons (TPH) Associated with Releases of JP-5 Jet Fuel (revised February 12, 2022)

The original January 27, 2022 memorandum was revised to clarify that TPH action levels apply to the sum of all detected TPH associated with the targeted fuel type. Clarification notes were also added regarding potential adjustment of Total TPH with respect to reported levels of BTEXMN and overlap of individual laboratory TPH test ranges. No revisions were made to Table 1 or to the attachment to the original January 27, 2022 memorandum.

Background

Total Petroleum Hydrocarbon (TPH) is defined as the sum total of all hydrocarbons and hydrocarbon-related degradation products not otherwise tested for and assessed as individual compounds (HIDOH 2017). Testing and assessment of individually targeted compounds, including benzene, toluene, ethylbenzene, xylenes, methylnaphthalenes and naphthalene (BTEXMN), is carried out concurrent with testing for TPH.

The Hawai'i Department of Health (HIDOH) has published a risk-based "action level" for "Total Petroleum Hydrocarbon (TPH)" associated with middle distillate, petroleum fuels of 400 ug/L (HIDOH 2017). As stated in the referenced guidance document, the action level is intended to reflect the toxicity of degraded, non-volatile, dissolved-phase diesel in water. The action level is not applicable to releases of fuel directly into a drinking water system where volatile contaminants might still be present.

In the case of such releases, an independent TPH action level must be developed that reflects the specific type of fuel released and takes into consideration exposure via inhalation of vapors during use of impacted water. This technical memorandum specifically presents toxicity-based, tapwater action levels for TPH in water that has been impacted by JP-5 jet fuel and serves as an addendum to the HIDOH Environmental Action Level guidance (HIDOH 2017).

Methods

Details of the calculation of the action level are provided in the attachment to this memorandum. In summary, a six-step approach was used:

- Step 1:** Estimation of the carbon range and BTEXMN makeup of fresh, JP-5 jet fuel;
- Step 2:** Estimation of the dissolved-phase makeup of carbon range and BTEXMN compounds in water that is in direct contact with fresh JP-5 jet fuel;
- Step 3:** Calculation of the weighted toxicity of the carbon range component of the dissolved-phase mixture, assumed to represent non-degraded compounds reported as "TPH;"
- Step 4:** Calculation of the weighted toxicity of the combined carbon range-plus-BTEXMN component of the dissolved-phase mixture, assumed to represent non-degraded compounds reported as "TPH;"
- Step 5:** Calculation of weighted toxicity factors for dissolved-phase JP-5 based on different mixtures of non-degraded and degraded compounds; and
- Step 6:** Calculation of associated TPH action levels for dissolved-phase JP-5 TPH in tapwater based on toxicity factors derived in Step 5.

The tapwater model presented in the USEPA Regional Screening Level guidance document was used to derive TPH action levels (USEPA 2021). The model assumes near daily exposure of young children to dissolved-phase JP-5 in tapwater over six years through use of the water for drinking (ingestion) as well as bathing (dermal exposure). The tapwater model further assumes potential inhalation of vapors during use of the water (e.g., showering and use of dishwashers and washing machines).

Calculated Action Levels

Action levels for three scenarios of impacts to drinking water wells by JP-5 were developed (Table 1): 1) Fresh JP-5 product released in immediate vicinity of a well and minimal degradation of hydrocarbons in the water, 2) Impact to well by plume of mixed, non-degraded and degraded related hydrocarbons and 3) Impact to well by degraded, non-volatile plume of JP-5 contaminated water. The toxicity factors and default, exposure parameter values were incorporated into the USEPA Regional Screening Level guidance model for tapwater (USEPA 2021) to yield corresponding action levels of 211 µg/L, 313 µg/L and 447 µg/L for each scenario (see Table 1).

The action levels are anticipated to be protective of human health under normal use of tapwater in the absence of other contaminants in the water. Exceeding an action level indicates that additional evaluation of potential health risk is required (HIDOH 2017).

It is anticipated that the action level of 313 µg/L pertinent to water well impacts by a partially degraded plumes of JP-5 will be pertinent to most groundwater scenarios in Hawai'i. However, releases of fresh JP-5 in the immediate vicinity of a well with little time for degradation to occur before entering a drinking water system, however, require use of the more stringent action level of 211 µg/L. Use of the less stringent action level of 447 µg/L for plumes in which all hydrocarbons have been partially oxidized is not recommended in absence of an extensive monitoring network that confirms the absence of non-degraded hydrocarbons in the water.

Application

As a default, hydrocarbon-related degradation products are assumed to have a similar toxicity as the parent compounds (HIDOH 2017). Polar compounds should therefore not be removed from water samples using silica gel cleanup or other methods prior to testing.

The action levels apply to the sum of all hydrocarbons and hydrocarbon-related degradation products associated with JP-5 jet fuel. Note that "Total Petroleum Hydrocarbon" is normally divided into three separate ranges of compounds by the laboratory based on the boiling points of the individual compounds (low, mid and high). Low-boiling point compounds are often referred to as "gasoline range." Medium boiling point compounds are often referred to as "diesel range." High boiling point compounds are often referred to as "oil range." The example JP-5 action levels apply to the sum of detections for each individual range.

As feasible, data can be adjusted to take into account overlap between two ranges and subsequent double counting (e.g., overlap of C10-C12 compounds for reporting of "gasoline range" and "diesel range" compounds). This should be discussed with the laboratory ahead of time and the method used to adjust for overlap described in the project report.

Individually targeted BTEXMN compounds and other individually targeted compounds identified for the project must be tested for and assessed separately. Reported concentrations of individually targeted compounds can be subtracted from the concentration of TPH reported for the related fuel range in order to avoid double counting, provided that the same test method was used for both sets of data. For example, reported concentrations of BTEX can be subtracted from the reported concentration of TPH associated with gasoline-range compounds prior to calculation of a Total TPH concentration provided that Method 8260 was used for both sets of data.

Non-detects for individual TPH ranges do not need to be not considered in summing Total TPH, provided that the laboratory Method Detection Level (MDL) does not exceed the MDL upper limit established for the project.

Note that the calculated action levels are very near to and in some cases might be slightly under typical laboratory Method Reporting Levels (MRL) for TPH in water. Detections of TPH above the laboratory Method Detection Level (MDL) and above the recommended action level but below the laboratory MRL should be verified by a review of the chromatogram for the sample.

References

HIDOH, 2017, Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater – Hawaii Edition (Fall 2017): Hawai'i Department of Health, Office of Hazard Evaluation and Emergency Response.

<https://health.hawaii.gov/heer/guidance/ehe-and-eals>

USEPA, 2021, Regional Screening Levels: United States Environmental Protection Agency, Superfund, November 2021.

Table 1. Calculated action levels for TPH associated with JP-5 contaminated groundwater under different plume degradation scenarios.

Plume Degradation Scenario	JP-5 TPH Action Level	Notes
¹Non-Degraded	211 µg/L	Applies to groundwater impacted by releases of fresh product in immediate vicinity of a production well with minimal degradation of JP-5 related hydrocarbons before entering a drinking water system.
²Mixed	313 µg/L	Applies to partially degraded plumes that include a mixture of degraded and non-degraded JP-5 related hydrocarbons (considered applicable to most aged releases of JP-5).
³Degraded	447 µg/L	Applies to plumes where all hydrocarbons have undergone some degree of degradation and are no longer significantly volatile (requires extensive monitoring to support degradation state and use).

Notes

1. Assumes no degradation of hydrocarbons or associated reduction in volatility; considers exposure via ingestion, dermal contact and inhalation of vapors.
2. Assumes 50:50 mixture of non-degraded and degraded hydrocarbons with volatility of non-degraded compounds preserved; considers exposure via ingestion and dermal contact with reduced but still significant exposure via inhalation of vapors.
3. Assumes at least partial degradation of all hydrocarbons to non-volatile compounds and exposure via ingestion and dermal contact.

APPROVED

Kathleen Ho

Kathleen S. Ho
Deputy Director of Environmental Health

Feb 12, 2022

Date

Attachment 1: Derivation of JP-5 TPH Tapwater Action Level

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1.0. Conceptual Site Model

1.1 Groundwater Plume Degradation State Scenarios

Three scenarios of impacts to drinking water wells by JP-5 were considered: 1) Fresh JP-5 product released in immediate vicinity of a well and minimal degradation of hydrocarbons in the water, 2) Impact to well by plume of mixed, non-degraded and degraded related hydrocarbons and 3) Impact to well by degraded, non-volatile plume of JP-5 contaminated water. Under the first scenario, no degradation of hydrocarbons is assumed prior to the groundwater entering a drinking water system. The original volatility of the hydrocarbon compounds is retained. Exposure is assumed to occur via ingestion, dermal contact and inhalation of vapors. While rare, these scenarios pose the greatest risk to users of the water distribution system.

Under the second scenario, half of the original hydrocarbons in the dissolved-phase mixture are assumed to have partially degraded. These compounds are assumed to no longer be significantly volatile. Exposure to the mixture is assumed to occur via ingestion, dermal contact and inhalation of vapors associated with the non-degraded, parent hydrocarbons still present in the plume. Although simplistic, consideration of a 50:50 mixture of non-degraded and degraded compounds equally split between BTEXMN and aliphatic and aromatic carbon ranges is adequate for development of initial action levels. This scenario is considered applicable to most releases of JP-5 to groundwater, where sufficient time has lapsed and environmental conditions allow at least partial degradation of the original hydrocarbons.

The third scenario applies to an aged or otherwise weathered plume characterized by at least partial degradation of all hydrocarbons. The volatility of the resulting mixture is assumed to be minimal, with risk driven by ingestion and dermal contact. Consideration of this release and exposure scenario should be supported by extensive monitoring of the plume and testing to verify the absence of original and potentially still volatile, parent hydrocarbons.

1.2 Primary Receptors of Concern

The primary receptors of concern are young children. Exposure to petroleum in tapwater is assumed to occur via direct ingestion of tapwater, dermal contact during bathing and/or inhalation of vapors during bathing. Children, with their higher body surface area to size ratio are at particular risk for increased toxicity from dermal exposures. Dermal exposure to non-degraded petroleum in tapwater focuses the uptake of more soluble and less volatile aromatic carbon range compounds that could penetrate the skin during bathing. Undegraded, highly volatile aliphatic compounds are assumed to be rapidly emitted from the water due to characteristic, very high Henry's Law Constants and not available for dermal uptake (USEPA 2021). The volatility of degraded compounds is assumed to be relatively low and the inhalation pathway insignificant (Zemo et al. 2013; 2016). Degraded light-end carbon range compounds as well as degraded BTEXMN are, however, assumed to remain in the water and pose a dermal exposure risk.

1.3 Contaminants of Potential Concern (COPCs)

Noncancer health risk posed by dissolved-phase JP-5 in tapwater is assessed in terms of three components: 1) Individually targeted compounds such as benzene, toluene,

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ethylbenzene, xylenes, methylnaphthalenes and naphthalene (BTEXMN); 2) Non-specific compounds associated with aliphatic and aromatic carbon ranges and 3) Hydrocarbon-related degradation products. The latter includes complex mixtures of degradation products associated with the partial oxidation of BTEXMN- and carbon range compounds, sometimes referred to as “Hydrocarbon Oxidation Products (HOPs)” (Mohler et al. 2013; Zemo et al. 2013; CAEPA 2019). Under HIDOH guidance (HIDOH 2017), the sum total of non-degraded carbon ranges and hydrocarbon-related degradation products is collectively reported and assessed as “Total Petroleum Hydrocarbon (TPH).”

Cancer risk is assessed separately based on well-studied, individual compounds such as benzene, ethylbenzene and naphthalene and not addressed in this paper. These same compounds also pose noncancer health hazards and are included in consideration of exposure to degraded hydrocarbons in tapwater.

2.0 Methods

2.2 Predicted Makeup of Dissolved-Phase JP-5 in Water

The carbon range and BTEXMN makeup of dissolved-phase JP-5 in water that is in contact with fresh product can be initially estimated based on the weight percent and effective solubility of compounds in the parent fuel mixture. The effective solubility of individual components of a fuel is calculated in accordance with Raoult’s Law as (after O’Reilly et al. 2001):

$$C_i = x_i \times S_i \quad \text{Eq 1)}$$

where:

C_i = Effective solubility of the compound;

x_i = Mole fraction; and

S_i = Pure component solubility.

The mole fraction reflects the ratio of the number of moles of one component of a solution to the total number of moles representing all of the components, in this case TPH carbon ranges and BTEXMN, and is calculated as

$$x_i = \left[\frac{\frac{w_i \times 0.01}{MW_i}}{\frac{1}{MW_{ave}}} \right] \quad \text{Eq 2)}$$

where:

w_i = Weight percent of the constituent in the mixture (converted to a fraction);

MW_i = Average molecular weight of the constituent; and

MW_{ave} = Average molecular weight of the mixture.

The equation assumes that the total mass of the fuel is equal to one mole.

Equations 1 and 2 can be simplified to:

$$C_i = \left(\frac{w_i \times 0.01}{MW_i} \times MW_{ave} \right) \times S_i. \quad \text{Eq 3).}$$

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An average molecular weight for JP-5 fuel of 185 was assumed for the calculations (NRC 1996). This equation can be used to calculate effective solubilities for BTEXMN and carbon ranges based on published data for various fuel types. The effective solubilities are assumed to reflect the relative makeup of dissolved-phase hydrocarbons in water that is in direct contact with fresh product.

2.3 Calculation of Weighted Toxicity Factors

Weighted Harmonic Means

Physiochemical constants and toxicity factors for BTEXMN and carbon ranges compounds are provided in Table 1. The harmonic mean weighted to the relative proportion of targeted compounds in a mixture is used to calculate weighted toxicity factors for dissolved-phase mixtures (ORDEQ 2003). Use of the harmonic mean rather than arithmetic average biases the results to the more toxic component of the mixture. Weighted toxicity factors for non-degraded JP-5 compounds consider only the non-BTEXMN carbon range fraction of the mixture. Remaining BTEXMN compounds are assumed to be tested for and assessed separately. The weighted toxicity of degraded mixtures is, in contrast, based on the relative proportion of the combined carbon range and BTEXMN compounds in the original mixture.

Weighted Toxicity Factors

Weighted, oral Reference Doses (RfDs) are calculated as:

$$\text{Weighted RfD}_{\text{oral}} \text{ (mg/kg-day)} = \frac{1}{\left[\frac{(\% \text{ Fraction A})}{\text{Fraction A RfD}_{\text{oral}}} + \frac{(\% \text{ Fraction B})}{\text{Fraction B RfD}_{\text{oral}}} + \text{etc.} \right]} \quad \text{Eq 4)}$$

where:

- % Fraction "X" = Percent makeup of the subject carbon range fraction +/- BTEXMN relative to the total concentration of measured carbon ranges;
- Fraction "X" Toxicity Factor: Toxicity factor assigned to subject carbon range fraction +/- BTEXMN.

Weighted toxicity factors for dermal exposure are calculated using a similar approach:

$$\text{Weighted RfD}_{\text{dermal}} \text{ (mg/kg-day)} = \frac{1}{\left[\frac{(\% \text{ Fraction A})}{\text{Fraction A RfD}_{\text{dermal}}} + \frac{(\% \text{ Fraction B})}{\text{Fraction B RfD}_{\text{dermal}}} + \text{etc.} \right]} \quad \text{Eq 5)}$$

Dermal toxicity factors for non-degraded mixtures focus on more soluble and less volatile, C13+ aromatic compounds. Calculation of weighted, dermal toxicity factors for degraded mixtures again requires consideration of combined, original carbon range and BTEXMN mixture.

Weighted Reference Concentrations (RfCs) applicable to the inhalation exposure focus on volatile aromatic and aliphatic carbon ranges but were otherwise calculated in a similar manner:

$$\text{Weighted RfC} \text{ (}\mu\text{g/m}^3\text{)} = \frac{1}{\left[\frac{(\% \text{ Fraction A})}{\text{Fraction A RfC}} + \frac{(\% \text{ Fraction B})}{\text{Fraction B RfC}} + \text{etc.} \right]} \quad \text{Eq 6)}$$

Inhalation toxicity factors for non-degraded compounds focus on the relative makeup of volatile, C5-C12 aliphatic and C9-C12 aromatic carbon ranges in the dissolved-phase

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mixture. Inhalation toxicity factors are again not calculated for HOPs mixtures, since degraded carbon range and BTEXMN compounds are assumed to be of low volatility.

3.0 USEPA Tapwater Model

The tapwater model presented in the United States Environmental Protection Agency (USEPA) Risk-Based Screening Level (RSL) *User's Guide* document is used to calculate action levels for TPH associated with undegraded and degraded plumes of petroleum-contaminated water (USEPA 2021). Model equations are provided in the USEPA document.

3.1 Default Parameter Values

Exposure parameter values used in the USEPA tapwater model that are not specific to individual chemicals are summarized in Table 2. Parameter values reflect exposure assumptions for assessment of noncancer health hazards posed to children age 0 to 6 years old. Consideration of exposure of young children to contaminants in drinking water is assumed in the model to be protective of adults and other sensitive populations as well. Assessment of the ingestion and inhalation exposure pathways is relatively simple and focuses on the volume of tapwater consumed and indoor air inhaled per day by young children. Default ingestion rate and inhalation rate values noted in Table 2 were taken directly from the USEPA (2021) RSL guidance. A gastrointestinal absorption factor of "1" was used in the tapwater model for all compounds (i.e., 100% of compound available for absorption).

An exception to use of default, USEPA model assumptions is the period of time per day that residents might be exposed to volatile contaminants emitted to indoor air during use of showers, dishwashers, washing machines and similar indoor activities. The USEPA tapwater model assumes that these activities are carried on 24 hours a day with a single, instantaneous exchange of indoor air at the beginning of the next day. This is reflected in the model by use of a default, Resident Exposure Time to vapors in indoor air of 24 hours per day.

This assumption is excessively conservative. A more realistic Resident Exposure Time of 4.2 hours per day was selected for use in this memorandum. This assumes use of a shower by four residents for 0.54 hours each per day (USEPA 2021) and use of a dishwasher and laundry washing machine for one hour each per day. The default Exposure Frequency of 350 days per year and childhood Exposure Duration of six years used in the USEPA tapwater models were retained.

3.2 Weighted Dermal Exposure Parameter Values

Incorporation of the dermal contact pathway into the USEPA tapwater model for TPH and HOPs requires calculation of carbon range- and carbon range + BTEXMN-weighted values for several additional parameters. A detailed overview of the dermal exposure models is presented in USEPA (2004). Four chemical-specific parameters specific to dermal contact are utilized in the USEPA tapwater model (USEPA 2021):

- B: Dimensionless ratio of the permeability coefficient of a compound through the stratum corneum relative to its permeability coefficient across the viable epidermis = Chemical specific;
- T_{event} : Dermal absorption lag time per event (hours/event) = chemical specific;

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- t^* : Time to reach absorption steady-state (hours) = $2.4 \times T_{even}$;
- KP: Dermal permeability constant (centimeters/hour).

A summary of published and calculated dermal parameter values for targeted individual compounds and carbon ranges is provided in Table 3. Parameter values for targeted carbon ranges and BTEXMN compounds were taken directly from the USEPA (2021) RSL guidance. Parameter values for both C9-C12 aromatics and C13-C22 aromatics are based on the default values presented for “Aromatics Medium,” defined as C9-C16. These values, rather than less conservative values for “Aromatics High” (C17-C32) category, are applied to the full range of C13-C22 aromatics due to the anticipated predominance of smaller aromatics compounds in dissolved-phase mixtures.

Weighted harmonic mean dermal exposure factors for no-degraded and degraded JP-5 mixtures are calculated in the same manner as done for weighted toxicity factors:

$$\text{Dermal Parameter (units vary):} = \frac{1}{\left[\frac{(\% \text{ Fraction A})}{\text{Fraction A Parameter Value}} + \frac{(\% \text{ Fraction B})}{\text{Fraction B Parameter Value}} + \text{etc.} \right]} \quad \text{Eq 7}$$

where:

- % Fraction X = Percent makeup of the subject carbon range fraction +/- BTEXMN relative to the total concentration of measured carbon ranges;
- Fraction X Toxicity Factor: Dermal absorption parameter value assigned to subject carbon range fraction +/- BTEXMN.

4.0 Predicted, Relative Makeup of Dissolved-Phase Plume

4.1 Parent Fuel Makeup and Effective Solubility of COPCs

Table 4 presents the molecular weight, pure component solubility and average BTEXMN and aliphatic and aromatic carbon range makeup of JP-5. The default makeup of JP-5 neat fuel is based on summary review of Department of Defense military fuel specification requirements (USDOD 1998, 2004, 2016) provided by the US Navy (Mumly 2021). Although benzene is not intentionally included in JP-5 fuel, a default content of 0.03% is assumed to account for possible contamination of JP-5 from residual gasoline in refinery pipelines (CAEPA 2012; default content assumed for diesel fuels and current formulations for gasoline).

The effective solubility of BTEXMN and default, aliphatic and aromatic carbon ranges calculated using Equation 3 is included in Table 4. The effective solubilities are, for the purposes of this document, assumed to reflect the makeup of dissolved-phase hydrocarbons in immediate, direct contact with fresh JP-5 product. Compounds not related to BTEXMN and specified carbon ranges are assumed to make up a minimal part of the fuel. The sum of the calculated, effective solubilities predicts a concentration of dissolved-phase hydrocarbons in water in contact with fresh JP-5 of 29 mg/L (see Table 4). This likely over predicts the concentration of JP-5 ever to be detected in water samples due to dilution as dissolved-phase compounds diffuse away from free product.

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4.2 Predicted Makeup of Dissolved-Phase Hydrocarbons

In Table 5, the effective solubility of the individual components in JP-5 is used to predict the relative BTEXMN and carbon range makeup of dissolved-phase JP-5 in water that is in direct contact with fresh fuel. Table 6 presents the makeup of dissolved-phase hydrocarbons in terms of the risk-based carbon ranges noted in Table 2. The result is assumed to represent the initial hydrocarbon composition of groundwater impacted by a fresh release of JP-5 fuel. The composition of the plume will change over time as the parent hydrocarbons begin to partially degrade. This will affect both the volatility and the weighted toxicity of compounds collectively tested for and reported as “TPH.”

5.0 Calculation of Weighted Toxicity Factors

Table 7 summarizes weighted oral, dermal and inhalation toxicity factors for non-degraded and degraded TPH associated with JP-5 based on the relative makeup of dissolved-phase carbon range and BTEXMN noted in Table 6 and the three degradation scenarios described in Section 4.0. Toxicity factors pertinent to each degradation scenario are subsequently used to calculate a corresponding TPH (JP-5) tapwater action level for that specific scenario.

5.1 Non-Degraded and Degraded JP-5 Mixtures

A weighted, oral Reference Dose (RfD) of 0.030 mg/kg-day is calculated using Equation 4 for the predicted mixture of aliphatic and aromatic, carbon range compounds noted in Table 6 (see Table 7). A dermal RfD of 0.034 mg/kg-day is calculated using Equation 5. Equation 6 yields an inhalation Reference Concentration of 0.111 mg/m³. These toxicity factors are assigned to TPH associated with non-degraded JP-5 mixtures.

An oral RfD of 0.036 is calculated for a combined mixture of dissolved-phase carbon range compounds and BTEXMN. The dermal RfD is assumed to be equivalent to the oral RfD, since degraded compounds are assumed to be non-volatile and have 100% absorption. These toxicity factors are assigned to TPH associated with non-degraded JP-5 mixtures. An inhalation RfC is not applicable since volatilization to air during use of the water is assumed to be minimal in comparison to exposure via direct ingestion and dermal contact.

5.2 50:50 Mixtures of Non-Degraded and Degraded Compounds

Plumes of petroleum-contaminated water are normally a mixture of undegraded and partially degraded compounds (HIDOH 2018; ITRC 2018). Weighted TPH toxicity factors for such mixed plumes can be calculated in the same manner as used for individual constituents based on Equations 4-7.

A 50:50 mixture of undegraded and degraded compounds is used as a default. This is reflected in Equations 4-6 by consideration of weight-percent makeup of 50% for both non-degraded TPH mixtures and degraded TPH mixtures. A final, oral RfD of 0.033 mg/kg-day is calculated based on the toxicity factor calculated for each type of mixture (see Table 7). A dermal RfD of 0.035 mg/kg-day and an inhalation RfC of 0.221 mg/m³ are similarly calculated.

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6.0 Calculation of Tapwater Action Levels

Risk-based TPH action levels calculated for the three, JP-5 plume degradation scenarios are summarized in Table 8. Weighted toxicity factors estimated for the parent, aliphatic-aromatic carbon range makeup of dissolved-phase hydrocarbons associated with JP-5 generated a risk-based action level for TPH of 211 µg/L based on the USEPA Tapwater screening level model. Toxicity factors estimated for a 50:50 mixture of non-degraded and degraded, dissolved-phase JP-5 in water yielded a TPH action level of 313 µg/L. Consideration of the oral and dermal toxicity factors estimated for plume where all parent hydrocarbons have partially degraded yielded a TPH action level of 447 µg/L.

The inclusion of degraded benzene in calculation of TPH action levels for the latter two plume scenarios increases the predicted overall oral and dermal toxicity of the plume by approximately 20% and reduces the action level by a similar amount. This is considered a conservative but necessary adjustment in the absence of more detailed data for a specific fuel release.

7.0 Comparison to Predicted Toxicities of Degraded Hydrocarbon Plumes

Zemo et al. (2016) evaluate the composition and toxicity of diesel-related metabolites in groundwater at different stages of degradation. This offers an alternative approach for assessment of health risk posed by fully degraded plumes of petroleum-contaminated water (HIDOH 2018). The suitability of the toxicity classification approach for petroleum-related metabolites is debated (CAEPA 2016; Hellmann-Blumberg et al. 2016; O'Reilly 2016; CRCC 2018). Preliminary recommendations presented by Zemo et al. (2016) are the most comprehensive to date and are a useful starting point for assessment of the weighted toxicity of metabolites in comparison to the parent, hydrocarbon compounds.

Five "polar families" or suites of metabolite-related alcohols, esters/acids, ketones, aldehydes and phenols were designated by Zemo et al. (2016; see also Zemo et al. 2013). Compounds within each suite were assigned a toxicity ranking of "Low" (RfD 0.1 to 1.0 mg/kd-day), "Low-Moderate" (RfD 0.01 to 0.1 mg/kd-day) or "Moderate" (RfD 0.001 to 0.01 mg/kd-day). Alcohols and acids/esters were predicted to be the least toxic of the metabolites. Ketones include a mix of low-toxicity and low-moderate toxicity compounds. Aldehydes were assumed to be of low-moderate toxicity. Phenols were assumed to have a moderate toxicity.

Progressive degradation of plumes of petroleum-contaminated water were predicted by Zemo et al. (2016) to be characterized by specific combinations of individual metabolites and metabolite suites (HIDOH 2018). Stage 1 degradation mixtures include a modest proportion (22%) of Low-Moderate and Moderate toxicity ketones and aldehydes. Undegraded, dissolved hydrocarbons, including BTEXMN, were assumed to still be present within the plume. As degradation proceeds, the plume was predicted to become progressively more dominated lower toxicity acids and esters as degradation continues.

Although not discussed by Zemo et al. (2016), a logical, next step is to calculate a corresponding range of weighted toxicity factors for each degradation stage (HIDOH 2018). This can be accomplished in the same manner as done for carbon range and BTEXMN mixtures discussed earlier in this paper. An oral RfD of 0.02 mg/kg-day for degraded diesel is calculated for Stage 1 metabolite mixture based on the lowest of range

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of toxicities proposed for individual metabolite suites (see HIDOH 2018). This is somewhat lower (higher toxicity) than the oral toxicity factor of 0.036 mg/kg-day calculated for degraded JP-5 noted in Table 7. A higher toxicity of dissolved-phase diesel is expected, however, due to the absence of lower-toxicity, C5-C8 aliphatic compounds in diesel fuel that are otherwise found in JP-5 and “dilute” the more toxic, degraded BTEXMN and heavier aromatic compounds that would be found in a dissolved-phase, diesel mixture.

The toxicity of hydrocarbon-related metabolite mixtures estimated based on Zemo et al. (2016) was predicted to decrease by a factor of up to three with increasing degradation and a progressive dominance of less toxic acids and esters. This suggests that the dissolved-phase makeup and weighted toxicity factors presented in Table 7 might be overly conservative for tapwater impacted by heavily degraded JP-5 compounds. A more detailed, site-specific analysis of both the chemistry and toxicity of degraded compounds would be required to further investigate this issue.

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Table 1. Example physiochemical constants and toxicity factors for BTEXMN and TPH carbon ranges.

¹ Chemical/ Carbon Range	Molecular Weight	² Vapor Pressure (mmHg)	Solubility in Water (µg/L)	Henry's Constant (unitless)	Partition Coeff, K _{oc} (cm ³ /g)	Diffusion Coefficient (cm ² /s)		³ RfD _{Oral} (mg/kg-day)	³ RfC _{inh} (µg/m ³)	
						air	water			
Benzene	78	95	1,790	0.23	146	0.09	1.0E-05	0.004	30	
Toluene	92	28	526	0.27	234	0.08	9.2E-06	0.08	5,000	
Ethylbenzene	106	9.6	169	0.32	446	0.07	8.5E-06	0.1	1,000	
Xylenes (total)	106	8.0	106	0.27	383	0.07	8.5E-06	0.2	100	
Naphthalene	128	0.085	31	0.018	1,544	0.06	8.4E-06	0.02	3	
Volatile Carbon Ranges	C5-C8 Aliphatics	93	76	11,000	54	2,265	0.08	1 x 10 ⁻⁵	0.04	600
	>C8-C12 Aliphatics	120	2.2	51,000	0.33	1,778	0.07	1 x 10 ⁻⁵	0.01	100
	C9-C10 Aromatics	170	0.11	10	4,900	680,000	0.07	5 x 10 ⁻⁶	0.03	100
Nonvolatile Carbon Ranges	>C12-C18 Aliphatics	280	0.0008	0.0015	110	4.0 x 10 ⁸	-	-	0.01	100
	>C18-C36 Aliphatics	120	2.2	51,000	0.33	1,778	0.07	1 x 10 ⁻⁵	3.0	nv
	>C10-C22 Aromatics	150	0.024	5,800	0.03	5,000	0.06	1 x 10 ⁻⁵	0.03	100

1. BTEXMN constants from USEPA (2021). Solubility based on a temperature of 25°C. Carbon range constants from Massachusetts Department of Environmental Protection (MADEP 2002) except constants from C19-C36 Aliphatics (Gustafson et al., 1997; based on EC>16-35 aliphatics in Table 7). USEPA (2009) RfD and RfC for "high flash naphtha" referenced for C9+ aromatics.
2. Carbon range vapor pressures converted from atmospheres (1atm = 760 mmHg).
3. Toxicity factors for BTEXMN from USEPA Regional Screening Levels guidance (USEPA 2021). Carbon range reference doses and concentrations from USEPA (2009) unless noted (see also HIDOH 2017). C5-C8 aliphatics RfD from MADEP (2003). C19+ aliphatics not significantly volatile.

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Table 2. Exposure parameter values and assumptions selected for calculation of TPH tapwater action levels.

Parameter	Abbreviation	Unit	¹Value
Skin Area - child	SAres-c	cm ²	6,365
Volatilization Factor	K	L/m ³	0.5
Water ingestion rate - children	IRWc	L/d	0.78
² Exposure Time - residents	ET	hr/day	4.2
Exposure frequency - residents	EFr	d/y	350
Exposure duration - residents total	EDr	yrs	26
Exposure duration - children	EDc	yrs	6
Body weight - child	BWc	kg	15
Averaging time (years)	AT	yrs	70
Days/year conversion	-	d/yr	365
Target Hazard Quotient	THQ	-	1.0

Notes:

1. USEPA (2021) default tapwater exposure values except as noted.
2. Based on assumed daily use of showers and dishwashers (see Section 2.1).

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Table 3. Chemical-specific parameter values selected for assessment of the dermal contact pathway.

Chemical	B (unitless)	T_{event} (hr/event)	t* (hr)	KP (cm/hr)	Basis
Benzene	0.05	0.29	0.69	0.01	USEPA (2004, 2021) default benzene values
Toluene	0.11	0.35	0.83	0.03	USEPA (2004, 2021) default toluene values
Ethylbenzene	0.20	0.41	0.99	0.05	USEPA (2004, 2021) default ethylbenzene values
Xylenes (Total)	0.20	0.41	0.99	0.05	USEPA (2004, 2021) default naphthalene values
Naphthalene	0.20	0.55	1.3	0.05	USEPA (2004, 2021) default naphthalene values
C6-C8 Aliphatics	0.72	0.32	1.2	0.20	USEPA (2021) default Aliphatic Low values
>C8-C12 Aliphatics	7.4	0.55	2.5	1.70	USEPA (2021) default Aliphatic Medium values
>C12-C18 Aliphatics	7.4	0.55	2.5	1.70	USEPA (2021) default Aliphatic Medium values
>C18 Aliphatics	9.8	0.95	4.3	1.96	USEPA (2021) default Aliphatic High values
C9-C12 Aromatics	0.31	0.60	1.4	0.069	USEPA (2021) default Aromatics Medium values
>C12-C22 Aromatics	0.31	0.60	1.4	0.069	USEPA (2021) default Aromatics Medium values
TPH (JP-5) Undegraded	0.490	0.749	1.960	0.111	¹ Calculated based on predicted carbon range makeup of dissolved-phase, undegraded TPH
TPH (JP-5) Degraded	0.211	0.483	1.181	0.054	¹ Calculated based on predicted carbon range + BTEXMN makeup of dissolved-phase, degraded TPH
TPH (JP-5) 50:50 Degradation	0.294	0.587	1.474	0.072	¹ Calculated based on 50:50 mixture of undegraded and degraded TPH

- Notes:
1. Refer to Tables 5-6 for a summary of the predicted carbon range and BTEXMN makeup of dissolved-phase TPH-related compounds in water that is in contact with fresh JP-5 fuel.

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Table 4. Estimated carbon range and BTEXMN makeup of JP-5 jet fuel and theoretical effective solubility of fuel-related components in water in contact with fresh fuel.

Chemical/ Carbon Range	¹ Molecular Weight	¹ Pure Component Solubility (mg/L)	² Average Weight % in Neat Fuel	³ Effective Solubility (mg/L)
Benzene	78	1,780	0.03%	0.72
Toluene	92	526	0.10%	0.60
Ethylbenzene	106	169	0.00%	-
Xylenes	106	178	4.6%	8.0
1-Methylnaphthalene	142	25.8	3.5%	0.67
2-Methylnaphthalene	142	24.6	0.00%	-
Naphthalene	128	31	3.0%	0.76
C5-C6 Aliphatics	81	36	0.00%	-
>C6-C8 Aliphatics	100	5.4	12%	0.67
>C8-C10 Aliphatics	130	0.43	16%	0.06
>C10-C12 Aliphatics	160	0.03	23%	0.01
>C12-C16 Aliphatics	200	7.6E-04	29%	0.00
>C16-C21 Aliphatics	270	2.5E-06	0.00%	0.00
>C21-C32 Aliphatics	400	1.5E-11	0.00%	0.00
>C8-C10 Aromatics	120	65	9.0%	5.2
>C10-C12 Aromatics	130	25	0.00%	0.00
>C12-C16 Aromatics	150	5.8	0.00%	0.00
>C16-C21 Aromatics	190	0.65	0.00%	0.00
>C21-C32 Aromatics	240	6.6E-03	0.00%	0.00
Sum BTEXMN:			11%	19
Sum Carbon Ranges:			89%	10
Sum BTEXMN+ Carbon Ranges:			100%	29

Notes:

1. Constants for BTEXMN from USEPA (2021). Constants for carbon ranges after values presented in California LUFT Manual (CAEPA 2012; see also HIDOH 2017).
2. Default makeup of JP-5 neat fuel based on summary review of Department of Defense military fuel specification requirements (USDOD 1998, 2004, 2016) provided by the US Navy (Mumly 2021). Default benzene content of 0.03% included to account for possible contamination of JP-5 from gasolines in refinery pipelines.
3. See Equation 3 in text. Based on assumed average molecular weight of JP-5 of 185 (NRC 1996).

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Table 5. ¹Theoretical, relatively makeup of dissolved-phase hydrocarbon mixture in water based on effective solubilities of components in fresh JP-5 at saturation (refer to Table 4).

Chemical/ Carbon Range	²Relative Carbon Range Makeup of Dissolved-Phase Hydrocarbons	³Relative BTEXMN Makeup of Dissolved-Phase Hydrocarbons	⁴Relative Volatile Carbon Range Makeup of Dissolved-Phase Hydrocarbons	⁵Relative CR+BTEXMN Makeup of Dissolved-Phase Hydrocarbons
Total BTEXMN				65%
Total Aliphatic Carbon Ranges				4.4%
Total Aromatic Carbon Ranges				30.9%
Benzene		7%		4.3%
Toluene		6%		3.6%
1-Methylnaphthalene		6.2%		4.0%
Xylenes		75%		48%
Naphthalene		7.08%		4.6%
C5-C6 Aliphatics	0%		0%	0.0%
>C6-C8 Aliphatics	11.4%		11.4%	4.02%
>C8-C10 Aliphatics	0.95%		0.95%	0.34%
>C10-C12 Aliphatics	0.09%		0.09%	0.03%
>C12-C16 Aliphatics	0.00%			0.00%
>C16-C21 Aliphatics	0.00%			0.00%
>C21-C32 Aliphatics	0.00%			0.00%
>C8-C10 Aromatics	88%		88%	30.9%
>C10-C12 Aromatics	0.0%		0.0%	0.00%
>C12-C16 Aromatics	0.00%			0.00%
>C16-C21 Aromatics	0.00%			0.00%
>C21-C32 Aromatics	0.00%			0.00%

Notes

1. Theoretical makeup of dissolved-phase hydrocarbons assuming fresh spill in direct contact with fresh JP-5 fuel and individual components present in water at maximum effective solubility.
2. Relative makeup of dissolved-phase carbon ranges.
3. Relative makeup of dissolved-phase, BTEXMN compounds.
4. Relative makeup of dissolved-phase, volatile carbon range compounds (C5-C8 aliphatics, >C8-C12 aliphatics, >C8-C12 aromatics).
5. Combined carbon range and BTEXMN components.

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Table 6. ¹Theoretical, relatively makeup of dissolved-phase hydrocarbon mixture in water based on effective solubilities of components in fresh JP-5 at saturation and grouped in terms of carbon range toxicity factors (refer to Table 1, Table 4 and Table 5).

Chemical/ Carbon Range	²Relative Hydrocarbon Makeup of Neat Fuel	³Relative Carbon Range Makeup of Dissolved-Phase Hydrocarbons	⁴Relative BTEXMN Makeup of Dissolved-Phase Hydrocarbons	⁵Relative Volatile Carbon Range Makeup of Dissolved-Phase Hydrocarbons	⁶Relative CR+BTEXMN Makeup of Dissolved-Phase Hydrocarbons
Total BTEXMN:	11%				65%
Total Carbon Ranges:	89%				35%
Benzene	0.03%		6.7%		4.3%
Toluene	0.10%		5.6%		3.6%
Ethylbenzene	0.0%		0.00%		0.00%
Xylenes	4.6%		75%		48%
1-Methylnaphthalene	3.5%		6.2%		4.0%
2-Methylnaphthalene	0.00%		0.00%		0.00%
Naphthalene	3.0%		7.1%		4.6%
C5-C8 Aliphatics	51%	11%		11%	4.0%
>C8-C18 Aliphatics	38%	1.0%		1.0%	0.37%
>C18-C32 Aliphatics	0.00%	0.00%		0.0%	0.00%
>C8 Aromatics	0.00%	88%		88%	31%
Sum:	100%	100%	100%	100%	100%

Notes

1. Theoretical makeup of dissolved-phase hydrocarbons assuming fresh spill in direct contact with fresh JP-5 fuel and individual components present in water at maximum effective solubility.
2. Refer to Table 4.
3. Relative makeup of dissolved-phase carbon ranges (used to derive weighted oral and dermal toxicity factors for non-degraded TPH compounds in Table 7).
4. Relative makeup of dissolved-phase, BTEXMN compounds (for general reference only).
5. Relative makeup of dissolved-phase, volatile carbon range compounds; used to derive weighted inhalation toxicity factor for non-degraded TPH compounds in Table 7).
6. Combined carbon range and BTEXMN components (used to derive weighted oral and dermal toxicity factors for non-degraded TPH compounds in Table 7).

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Table 7. Calculated, weighted toxicity factors for ¹TPH associated with non-degraded, degraded and 50:50 mixtures of dissolved-phase JP-5 in tapwater.

TPH Category	² TPH Associated with Non-Degraded Dissolved-Phase JP-5			³ TPH Associated with Degraded Dissolved-Phase JP-5		⁴ TPH Associated with 50:50 Mixture Non-Degraded:Degraded Dissolved-Phase JP-5		
	Oral RfD (mg/kg-day)	Dermal RfD (mg/kg-day)	Inhalation RfC (mg/m ³)	Oral RfD (mg/kg-day)	Dermal RfD (mg/kg-day)	Oral RfD (mg/kg-day)	Dermal RfD (mg/kg-day)	Inhalation RfC (mg/m ³)
TPH (JP-5)	0.030	0.034	0.111	0.036	0.036	0.033	0.035	0.221

Notes

1. Total Petroleum Hydrocarbon (TPH) defined as sum of non-specific carbon range aliphatic and aromatic compounds and all hydrocarbon-related degradation products, including degradation products associated with BTEXMN.
2. Oral and dermal Reference Doses (RfDs) and Inhalation Reference Concentration (RfC) weighted with respect to carbon range makeup for fuel type noted in Table 6 (excludes BTEXMN). Intended to represent toxicity of TPH component of non-degraded, dissolved-phase fuel in water. Non-degraded BTEXMN assessed separately. Considers ingestion of drinking water, inhalation to vapors during water use and dermal contact during bathing. Volatile aliphatic compounds assumed lost during water use and not considered for dermal contact.
3. Weighted toxicity factors for combined carbon range plus BTEXMN makeup noted in Table 6. Intended to reflect toxicity of partially degraded hydrocarbons in water. Considers ingestion of drinking water and dermal contact during bathing. Degraded compounds assumed to not be significantly volatile and not available for exposure via inhalation. Degraded aliphatic compounds assumed to remain in water and be available for dermal contact during bathing.
4. Toxicity factors calculated for a 50:50 mixture of degraded and non-degraded TPH-related compounds.

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Table 8. Calculated action levels for TPH associated with JP-5 contaminated groundwater under different plume degradation scenarios.

Plume Degradation Scenario	JP-5 TPH Action Level
¹ Non-Degraded	211 µg/L
² Mixed	313 µg/L
³ Degraded	447 µg/L

Notes

1. Assumes no degradation of hydrocarbons or associated reduction in volatility; considers exposure via ingestion, dermal contact and inhalation of vapors.
2. Assumes 50:50 mixture of non-degraded and degraded hydrocarbons with volatility of non-degraded compounds preserved; considers exposure via ingestion and dermal contact with reduced but still significant exposure via inhalation of vapors.
3. Assumes at least partial degradation of all hydrocarbons to non-volatile compounds and exposure via ingestion and dermal contact.