Division of Spill Prevention and Response
**Technical Memorandum**
Contaminated Sites Program May 17, 2023

# Bulk Petroleum Hydrocarbon Noncancer Toxicity for Human Health Risk Assessments

## Summary

The Alaska Department of Environmental Conservation (DEC) Contaminated Sites Program (CSP) has reviewed updated toxicity publications for bulk (or total) petroleum hydrocarbons and provided recommendation for Human Health Risk Assessments (HHRAs) with the Alaska analytical petroleum methods (AK101, AK102, and AK103). CSP has determined that consistent with the February 1, 2018, *Risk Assessment Procedures Manual* (RAPM), updated toxicity data for bulk petroleum hydrocarbons from sources outlined in the toxicity hierarchy[1] should be used when conducting risk assessments at contaminated sites in Alaska. CSP recommends using toxicity data from Table 1, or other approved levels identified through consultation with CSP risk assessment staff.

## Purpose

The purpose of this technical memorandum is to recommend the bulk petroleum hydrocarbon toxicities that responsible persons may use while conducting a HHRA under 18 Alaska Administrative Code (AAC) 75.340(f). This technical memorandum also explains how CSP evaluated and selected the set of toxicities for the respective Alaska analytical petroleum methods carbon ranges.

## Background

This technical memorandum is needed because there has been updated toxicity data for use in calculating bulk petroleum hydrocarbon fraction risk in HHRAs since the Total Petroleum Hydrocarbon Criteria Working Group (TPHWG)'s *Volume 4, Development of Fraction Specific Reference Doses (RfDs) and Reference Concentrations (RfCs) for Total Petroleum Hydrocarbons (TPH)* in 1997. The RAPM outlines the method and hierarchy for determining toxicity data for single components when conducting a risk assessment. Since bulk petroleum hydrocarbon fractions are a mixture of thousands of chemicals, identifying appropriate toxicity data can be more complex than for most compounds.

## Action

CSP recommends that responsible persons preparing HHRAs use the toxicities shown below in Table 1. The use of alternative levels to those presented in Table 1 must be approved by CSP and should be developed in consultation and coordination with CSP's risk assessment staff, per subsection 3.3.1 of the RAPM.

Responsible persons should assume that each bulk petroleum hydrocarbon fraction consists of the following composition:

- Gasoline range organics (GRO): 50% aliphatic/50% aromatic,

[1] See RAPM subsection 3.3.1 for details about CSP's toxicity hierarchy.

- Diesel range organics (DRO): 60% aliphatic/40% aromatic, and
- Residual range organics (RRO): 70% aliphatic/30% aromatic.

Alternatively, responsible persons may determine site-specific percentages of aliphatic and aromatic fractions using an approved analytical method in consultation with the CSP's chemist.

To streamline the process for calculating risk, CSP recommends using the United States Environmental Protection Agency (USEPA) Regional Screening Level (RSL) calculator for the media with the petroleum hydrocarbon fractions that exceed the USEPA RSL screening levels. Users can select "yes" for the "select risk out" option and "site specific" and "user-provided" under the "select screening level choice". The calculator will allow the user to enter in the exposure concentration, replace the toxicity values with the respective values listed in Table 1, and update the exposure parameters as needed for generating the risk output.

*Table 1: Recommended Toxicities for Bulk Petroleum Hydrocarbon Fractions*

| TPH Fraction | Carbon Range | RfD (mg/kg•day) | Indicator Compound(s) | RfC ($mg/m^3$) | Indicator Compound(s) |
|---|---|---|---|---|---|
| **GRO Aliphatic** | C6 – C10 | 0.005 | Cyclohexane[1] | 0.4 | n-heptane[1] |
| **DRO Aliphatic** | C10 – C25 | 0.01 | Chronic midrange aliphatic hydrocarbon streams[1] | 0.1 | Chronic midrange aliphatic hydrocarbon streams[1] |
| **RRO Aliphatic** | C25 – C36 | 3 | White mineral oil | - | - |
| **GRO Aromatic** | C6 – C10 | 0.004 | Benzene[2] | 0.03 | Benzene[2] |
| **DRO Aromatic** | C10 – C25 | 0.04 | Various chemicals in the range[3] | 0.2 | C9 aromatic[3] |
| **RRO Aromatic** | C25 – C36 | 0.03 | Represents the fraction-specific RfD for the ≥C17 carbon range[3] | - | - |

Notes to the Table:
[1] Source is from USEPA (2022).
[2] Source is the most conservative of benzene, toluene, ethylbenzene, and xylene (BTEX) toxicities. A hazard index (HI) for BTEX can replace the GRO aromatic assessment as noted in USEPA (2022).
[3] Source is from TPHWG (1997) with comparison to Table 4.

The final output will include hazard quotients (HQs) for the various petroleum hydrocarbon fractions that are summed for all complete exposure pathways for their respective HI for total petroleum risk for each receptor assessed. Please note these risk calculations are only for the cumulative bulk total petroleum hydrocarbon risk to the receptor and presented separately from the individual contaminants for cumulative risk.

# Rationale

Crude oil and petroleum products are complex mixtures that consist of thousands of individual chemicals. Only a few individual chemicals are well characterized, and these represent a small fraction of the mixture. Assessing risk with just the few well characterized individual chemicals results in a large uncertainty for the exposure to the remaining chemicals in the complex mixture. In recognition of the large uncertainty in the assessment of risk for the whole-product chemical makeup in a petroleum hydrocarbon release, many regulatory agencies, including CSP and USEPA, have adopted an approach using aliphatic and aromatic petroleum hydrocarbon fractions.[2]

As stated in the RAPM, responsible persons can obtain risk-based screening levels from the most current USEPA RSL table for chemical contaminants based on screening requirements of a HQ of 0.1 and a cancer risk of $1 \times 10^{-6}$. The USEPA RSL tables are updated biannually and provide the most current information for risk screening. These tables contain bulk petroleum hydrocarbon fractions presented as:

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|---|---|
| Aliphatic low | Aromatic low |
| Aliphatic medium | Aromatic medium |
| Aliphatic high | Aromatic high |

These fractions are analogous to CSP's GRO (low), DRO (medium), and RRO (high) without the aliphatic and aromatic concentrations.

CSP uses the Alaska petroleum analytical methods to determine the concentrations of GRO, DRO, and RRO. The analytical methods categorize bulk petroleum hydrocarbons into specific carbon (C) ranges. AK101 (GRO) consists of C6 – C10; AK102 (DRO) C10 – C25; and AK103 (RRO) C25 – C36. The recommended assumptions for aliphatic/aromatic percentages are GRO: 50%/50%, DRO: 60%/40% and RRO: 70%/30% based on the higher aromatic percentage from the February 1, 2018, *DEC Procedures for Calculating Cleanup Levels* and assuming the remaining composition is aliphatic. These do not exactly match the USEPA RSL low, medium, and high aliphatic and aromatic carbon ranges, but they are sufficient for screening. The *USEPA RSL User's Guide* acknowledges the carbon ranges may not match carbon ranges from laboratory results for petroleum hydrocarbon fractions and the published screening tables are presented as quantifiers with low, medium, and high ranges for the aliphatic and aromatic fractions. The evaluation of the carbon ranges and indicator compounds used can be refined in the risk characterization for the HHRA.

The USEPA RSL and TPHWG RfDs and RfCs for the petroleum aliphatic and aromatic carbon ranges were reviewed for use; these values are provided below in Tables 2 and 3, respectively. CSP determined that the low aliphatic, medium aliphatic, and high aliphatic data in Table 2 are representative of GRO aliphatic, DRO aliphatic, and RRO aliphatic, respectively. This is because the carbon ranges between the USEPA RSL are similar to the carbon ranges in the TPHWG or the same indicator compound was used. However, the USEPA RSL does not list toxicity data for low aromatic and the source recommended using the HI from BTEX. Additionally, the carbon ranges of medium aromatic and high aromatic in the USEPA RSL differ greatly from the carbon ranges from the TPHWG.

[2] CSP's 18 AAC 75, Oil and Other Hazardous Substances Pollution Control regulations and USEPA Office of Research and Development documents assessing the complete mixture of aliphatic and aromatic hydrocarbons in USEPA (2009a) and USEPA (2022).

CSP determined that the benzene surrogate was appropriate for the low aromatic (GRO aromatic) as it is the most conservative of BTEX. However, the HI from BTEX may be used to replace the GRO aromatic concentration assessment with the benzene surrogate. For aromatic medium and aromatic high, additional sources were reviewed, as shown in Table 4, and CSP determined that the data were similar for applying the toxicity values for medium aromatic and high aromatic from TPHWG. CSP recognizes that the TPHWG high aromatic RfD is two orders of magnitude higher and no RfC is provided as compared with the USEPA RSL information in Table 2, CSP recommends that these differences are discussed in the uncertainty section of the HHRA.

*Table 2: EPA RSL Toxicities for Bulk Petroleum Hydrocarbon Fractions*[1]

| TPH Fraction | Carbon Range | RfD (mg/kg•day) | Indicator Compound(s) | RfC ($mg/m^3$) | Indicator Compound(s) |
|---|---|---|---|---|---|
| **Low Aliphatic** | C5 – C8 | 0.005 | Cyclohexane | 0.4 | n-heptane |
| **Medium Aliphatic** | C9 – C18 | 0.01[2] | Chronic midrange aliphatic hydrocarbon streams | 0.1[2] | Chronic midrange aliphatic hydrocarbon streams |
| **High Aliphatic** | C19 – C32 | 3[2] | White mineral oil | - | - |
| **Low Aromatic**[3] | C6– C8 | - | - | - | - |
| **Medium Aromatic** | C9 – C10 | 0.01 | Trimethylbenzene | 0.06 | Trimethylbenzene |
| **High Aromatic** | C10 – C32 | 0.0003 | Benzo[a]pyrene | 0.000002 | Benzo[a]pyrene |

Notes to the Table:
[1] The source of indicator chemicals is from USEPA (2022).
[2] Same indicator compounds as TPHWG (1997) with updated RfDs.
[3] USEPA (2022) recommends using the HI for BTEX toxicities for the low aromatic.

*Table 3: TPHWG Toxicities for Bulk Petroleum Hydrocarbon Fractions (1997)*

| TPH Fraction | Carbon Range | RfD (mg/kg•day) | Indicator Compound(s) | RfC ($mg/m^3$) | Indicator Compound(s) |
|---|---|---|---|---|---|
| **Low Aliphatic** | C5 – C8 | 5[1] | <53% n-hexane/ commercial hexane mixture | 18.4[1] | <53% n-hexane/ commercial hexane mixture |
| **Medium Aliphatic** | C9 – C16 | 0.1 | Studies on C9 – C16 | 1 | Studies on C9 – C16 |
| **High Aliphatic** | C17 – C35 | 2 | White mineral oil | - | - |
| **Low Aromatic** | C7 – C8 | 0.2 | Toluene | 0.4 | Toluene |
| **Medium Aromatic** | C9 – C16 | 0.04 | Various chemicals in the range | 0.2 | C9 aromatic |

| | | | | | |
|---|---|---|---|---|---|
| **High Aromatic** | C17 – C35 | 0.03 | Represents the fraction-specific RfD for the ≥C17 carbon range | - | - |

Notes to the Table:
[1] Commercial n-hexane was updated in USEPA (2009b) with the following recommendation: no usable information for a RfD and chronic RfC = 0.6 milligrams per cubic meter (mg/m$^3$).

*Table 4: Other Sources of Medium Aromatic and High Aromatic Toxicities for Bulk Petroleum Hydrocarbon Fractions*

| Reference | Carbon Range | RfD (mg/kg•day) | RfC (mg/m$^3$) |
|---|---|---|---|
| **ATSDR (1999)** | >EC16 – EC35 Aromatic | - | - |
| **Massachusetts DEP (2003)** | C9 – C10 Aromatic | 0.03 | 0.05 |
| | C11 – C22 Aromatic | 0.03 | - |
| **Washington DOE (2006)** | EC9 – EC10 Aromatic | 0.1 | 0.399 |
| | >EC10 – EC12 Aromatic | 0.02 | 0.003 |
| | >EC12 – EC16 Aromatic | 0.05 | 0.2 |
| | >EC16 –EC21 Aromatic | 0.03 | - |
| | >EC21 – EC34 Aromatic | 0.04 | - |
| **California EPA (2009)** | C9 – C16 Aromatic | 0.03 | 0.05 |
| | C17 – C32 Aromatic | 0.03 | - |
| **USEPA (2009a)** | C9 – C16 Aromatic | 0.03 | 0.1 |
| | C17 – C32 Aromatic | 0.04 | - |

## Regulatory Authority

The actions described in this technical memorandum are necessary to meet requirements of 18 AAC 75.340(f); RAPM, Section 3.1.4; and RAPM, Section 3.3.1.

## References


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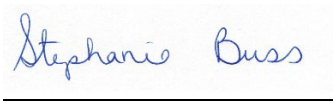

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