

Toxicity Data and Physical/Chemical Properties for Petroleum Mixtures

In 2006, the Washington State Department of Ecology (Ecology) developed Cleanup Levels and Risk Calculations (CLARC) guidance surrounding the use of noncancer reference doses (RfDs) to calculate Method B and C cleanup levels for petroleum mixtures. The 2006 guidance, which is titled *Reference Doses for Petroleum Mixtures*, is updated and superseded by the guidance provided herein. The updated information provided in this 2021 guidance has been incorporated into Ecology's Excel Workbook tool (MTCA TPH Ver. 11.1) for calculating cleanup levels for petroleum contaminated sites¹, and is to be used to establish cleanup levels for petroleum mixtures consistent with the Ecology's 2006-2007 CLARC guidance titled *Calculation of Method B and C Cleanup Levels for Petroleum Mixtures* (see Attachment 1). Tables 1 through 4, provided at the end of this guidance and listed below, contains updated toxicity criteria along with physical/chemical parameters for petroleum mixtures.

- **Table 1** Updated Noncancer Reference Doses For Total Petroleum Hydrocarbon (TPH) Fractions and Individual Hazardous Substances Related to TPH – Revised June 2021
- **Table 2** Updated Cancer Potency Factors (CPFs) For Individual Hazardous Substances Related to Total Petroleum Hydrocarbons (TPH) Revised June 2021
- **Table 3** Updated Physical/Chemical and Exposure Parameters For Total Petroleum Hydrocarbon (TPH) Fractions and Individual Hazardous Substances Related to TPH - Revised June 2021 (updated in August 2022).
- **Table 4** Model Toxics Control Act (MTCA) TPH Excel Workbook Tool (Ver. 11.1) Updated Chemical Database June 2021

Toxicity Data

Petroleum products are complex mixtures that include hundreds of compounds. Estimating the toxicity of such mixtures was subject to considerable discussion throughout the 2007 MTCA rule-making process, involving Ecology, the Washington State Department of Health (WDOH), the TPH Project Oversight Group (POG), the United States Environmental Protection Agency (EPA), and numerous stakeholders. Based on this work, consensus was reached on three principles:

- 1. Where RfDs and cancer potency factors (CPFs) are available for individual substances that are part of the petroleum mixture, these values should be used for these substances.
- 2. The remainder of the mixture should be divided into several groups of substances, or fractions, and an RfD assigned to each fraction based on known toxicological information about substances found in that fraction or on a chemical with similar structure.

¹ <u>https://ecology.wa.gov/Regulations-Permits/Guidance-technical-assistance/Clean-up-petroleum-contamination</u>



3. Because of the wide range of chemicals and potential health effects, the noncarcinogenic toxicity posed by the various fractions should be assumed to be additive for the purposes of estimating the toxicity of a petroleum mixture.

Based on information developed by the National TPH Criteria Working Group, it was determined that the mixture of substances should be split into two main groups – aliphatic hydrocarbons and aromatic hydrocarbons. Each of these main groups was then further subdivided into fractions with similar physical properties.

Historical Toxicity Updates – Ecology published an initial set of RfDs for petroleum mixtures in November 2001 as part of CLARC Version 3.1 (*see* **Attachment 2**). These RfDs were updated by Ecology in 2006 after EPA's National Center for Environmental Assessment (NCEA²), Superfund Technical Support Center (STSC), published the provisional risk assessment issue paper *Derivation Support Document for Total Petroleum Hydrocarbons* (SRC SF 01-031/10-16-2002) (*see* **Attachment 3**).

June 2021 Toxicity Updates – Updates to the 2006 RfDs are provided herein and are based in part on EPA's 2009 NCEA published Provisional Peer-Reviewed Toxicity Values (PPRTVs) for six fractions of petroleum hydrocarbons (EPA, 2009). Toxicity criteria from EPA's PPRTV program along with data from other toxicity sources, including EPA's Integrated Risk Information System (IRIS), were used to update the 2006 RfDs. In addition, cancer potency factors (CPFs) for individual petroleum related hazardous substances were also updated. Toxicity updates for RfDs and CPFs associated with petroleum mixtures are presented in Tables 1 and 2, respectively. Table 4 shows the MTCA TPH Excel Chemical Database Worksheet with the updated toxicity values in blue font. A summary of updates is provided below.

• Noncancer RfD Updates (see Table 1)

Aliphatic (Equivalent Carbon [EC]>5 to EC8) – Cyclohexane is used as the toxicity surrogate to represent these petroleum fractions. An inhalation noncancer toxicity criterion is available for cyclohexane in IRIS, and EPA has concluded that there is inadequate data to derive an oral RfD (IRIS, 2021). EPA also concludes that available information is not adequate for a route-to-route extrapolation from the inhalation pathway to the oral pathway for this chemical (IRIS, 2021; EPA, 2003). As a result, the oral RfD of 1.71 mg/kg-day has been removed.

Note: Cyclohexane is used as the surrogate for these fractions because n-hexane's contribution to overall toxicity is separately evaluated using its own RfD. Testing for n-hexane is required when volatile petroleum hydrocarbon (VPH) analysis is performed for Method B or C (MTCA Rule Table 830-1, Footnote 9³).

• Aliphatic (EC>8 to EC16) – Both the oral and inhalation RfDs were updated for these fractions based on information presented in EPA's 2009 PPRTV document for the

² The NCEA develops toxicity data in support of EPA's Provisional Peer-Reviewed Toxicity Value (PPRTV) program. NCEA is now known known as the Center for Public Health and Environmental Assessment (CPHEA) and is part of EPA's Office of Research and Development (ORD). PPRTV assessments are developed in response to requests from EPA's Superfund Program to the Superfund Health Risk Technical Support Center (STSC) located within the CPHEA. ³ <u>https://app.leg.wa.gov/WAC/default.aspx?cite=173-340-900</u>



medium range (EC>8 to EC16) aliphatic fraction (EPA, 2009). The oral and inhalation RfDs were updated to 0.01 and 0.0286 mg/kg-day, respectively.

- Aliphatic (EC>16 to EC34) The oral RfD was updated to 3 mg/kg-day for this fraction based on information presented in EPA's 2009 PPRTV document for white mineral oils (EPA, 2009).
- Aromatic (EC>12 to EC16) Both the oral and inhalation RfDs were updated for this fraction based on changes to toxicity data for 1,1-biphenyl. The oral RfD was updated to 0.5 mg/kg-day based on an updated IRIS value (IRIS, 2021). The inhalation RfD was updated to 1.14E-04 mg/kg-day based on a 2011 PPRTV value (EPA, 2011).
- Other Petroleum Related Hazardous Substances As shown in Table 1, noncancer RfDs were updated for the following chemicals: 1- and 2-methylnaphthalene, 1,2-dichloroethane (EDC), and benzo(a)pyrene. These updates are consistent with the toxicity data that is currently in Ecology's <u>CLARC database</u>⁴.
- Cancer CPF Updates (see Table 2)
 - As shown in Table 2, cancer CPFs were updated for the following chemicals: naphthalene, 1-methylnaphthalene, methyl-tert-butyl-ether (MTBE), ethylene dibromide (EDB), benzo(a)pyrene, and six other carcinogenic PAHs (by use of toxicity equivalent factors). These updates are consistent with the toxicity data that is currently in Ecology's CLARC database.

Note: Individual petroleum related hazardous substances with CPFs only, or CPFs in addition to RfDs, are evaluated independently for purposes of estimating cancer risks and calculating cleanup levels. Aliphatic and aromatic TPH fractions are evaluated based only on their noncancer additive effects.

Physical/Chemical Data and Exposure Parameters

Physical/chemical data that is currently utilized by Ecology's <u>MTCA TPH Excel Workbook Tool</u>⁵ were reviewed and updated to be consistent with Ecology's CLARC database. In addition, chemical-specific exposure parameters used to calculate risk-based soil and groundwater cleanup levels were reviewed and updated to be consistent with current EPA Risk Assessment Guidance for Superfund (RAGS). Updated physical/chemical data and exposure parameters are provided in **Table 3**. **Table 4** shows the MTCA TPH Excel Chemical Database Worksheet with the updated physical/chemical and exposure parameter values in blue font. A summary of the updates is provided below.

• **Physical/Chemical Values** – Physical/chemical parameters for establishing soil concentrations protective of groundwater through the use of the three- or four-phase partitioning models include: molecular weight (MW), water solubility (S), Henry's law (Hcc), soil organic carbonwater partitioning coefficient (Koc), and liquid density.

⁴ <u>https://ecology.wa.gov/Regulations-Permits/Guidance-technical-assistance/Contamination-clean-up-tools/CLARC/Data-tables</u>

⁵ <u>https://ecology.wa.gov/Regulations-Permits/Guidance-technical-assistance/Clean-up-petroleum-contamination</u>

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- Aliphatic and Aromatic Petroleum Fractions No changes were made.
 Physical/chemical values for the specific aliphatic and aromatic petroleum fractions are provided in Table 747-4 of the MTCA Rule.
- Individual Petroleum Related Hazardous Substances Physical/chemical parameters for the individual hazardous substances were updated to be consistent with Ecology's CLARC database. Values listed in the MTCA Rule (Tables 747-1 and 747-4) were used where available. Otherwise, parameter values from the <u>Oak Ridge National Lab (ORNL)</u> <u>Risk Assessment Information System (RAIS)</u>⁶ chemical database were used. Physical/chemical data in CLARC (except those listed in the MTCA Rule) have been updated to reflect values from the ORNL RAIS chemical database.
- Henry's law Temperature Adjustments Consistent with CLARC, data from ORNL RAIS, (i.e., boiling point, critical temperature, enthalpy of vaporization), along with formulas in EPA's Vapor Intrusion Screening Level (VISL) excel spreadsheet system⁷ (Chem Props worksheet), were used to adjust Henry's law based on 25° Celsius to 13° Celsius for the individual chemicals. This adjustment was made to better represent average Washington State shallow groundwater temperature. Henry's law for the petroleum fractions were taken from MTCA Table 747-4. The values were not adjusted to 13° Celsius as they are approximations that represent a range of chemicals. Also, other physical/chemical specific data needed to make the adjustment (e.g., critical temperature, boiling point) specific for these fractions have not been identified.
- **Exposure Parameters** Chemical-specific exposure parameters used to calculate risk-based soil and groundwater cleanup levels for petroleum mixtures include the groundwater inhalation correction factor (INH), the dermal absorption fraction (ABS), and the gastrointestinal absorption conversion factor (GI). Changes made to these factors are discussed below.
 - INH The INH is used to adjust exposure estimates based on ingestion of drinking water to take into account exposure to hazardous substances that are volatilized and inhaled during use of the water (e.g., washing and showering). According to the MTCA Rule, a value of 2 is used for volatile compounds, and 1 for all other substances. According to current EPA vapor intrusion (VI) guidance, a chemical is classified as being sufficiently volatile for the vapor pathway if its Henry's law constant is greater than 1 x 10⁻⁵ atm-m³/mol or its vapor pressure exceeds 1 millimeter of mercury (mm Hg) (EPA, 2015). Henry's law provides a measure of the extent of a chemicals ability to partition between air and water at equilibrium. The higher the Henry's law constant, the more likely a chemical is to volatilize than to remain in water.
 - Aliphatic and Aromatic Petroleum Fractions Ecology's current physical/chemical database for the MTCA TPH Excel Workbook Tool applies an INH of 1 (not volatile) for aliphatic and aromatic carbon fractions that are greater than EC12 (i.e., >EC12 to EC34). Based on a review of the Henry's law constants from these fractions, all of the aliphatic fractions significantly exceed a Henry's law of 1 x 10⁻⁵ atm-m³/mol. As a result, the assigned INH value for

⁶ <u>https://rais.ornl.gov/</u>

⁷ https://www.epa.gov/vaporintrusion/vapor-intrusion-database



aliphatic carbon fractions greater than EC12 to EC34 has been changed from 1 to 2. Aromatic carbon fractions up to EC21 also significantly exceed a Henry's law of 1×10^{-5} atm-m³/mol (by greater than 10 times). As a result, the assigned INH value for aromatic carbon fractions greater than EC12 to EC21 has been changed from 1 to 2. Aromatic carbon fractions greater than EC21 to EC34 are dominated by high molecular weight polycyclic aromatic hydrocarbons (PAHs) with Henry's law values less than 1×10^{-5} atm-m³/mol, and are not considered to be very volatile (EPA, 2009). As such, the INH value for this fraction remains at 1. These changes are consistent with EPA Superfund's Regional Screening Level (RSL) tables in which they assign all aliphatic and aromatic carbon fractions as volatile, with the exception of the aromatic 22-35 carbon range fraction (EPA, 2021).

- Individual Petroleum Related Hazardous Substances No changes were made to the INH factor for the individual petroleum related hazardous substances.
- Dermal Absorption Factor (ABS) Dermal ABS adjustments are used to estimate the amount of chemical that is absorbed from soil through the skin and into the blood stream. MTCA default ABS values provided in <u>WAC 173-340-740(3)(c)(iii)</u> were applied along with chemical-specific values from EPA's RAGS Part E, Supplemental Guidance for Dermal Risk Assessment (EPA, 2004), and values from the Agency for Toxic Substances and Disease Registry (ATSDR).
 - Aliphatic and Aromatic Petroleum Fractions Due to their makeup of volatile chemicals, all aliphatic carbon ranges, along with aromatics up to EC12, were assigned an ABS of 3%. The ABS value for aromatic carbon ranges greater than EC12 to EC34 remained at 10% based on the presence of semi-volatile chemicals.
 - Individual Hazardous Substances The ABS for 1- and 2-methylnaphthalene was changed to 13%, which is the chemical-specific value for PAHs (see Exhibit 3-4 of RAGS Part E; EPA, 2004). The ABS for n-hexane was changed to 0.05% because it has a higher vapor pressure than benzene. MTBE was also assigned an ABS of 0.05%.
- Gastrointestinal Absorption Conversion Factor (GI) Published toxicity data are not available for the dermal exposure route. To evaluate the dermal pathway, the oral toxicity factor is adjusted if necessary to represent an absorbed dose rather than an administered dose. The GI factor adjusts the orally administered dose for the amount absorbed since dermal exposure doses are expressed as "absorbed" doses. The adjustment accounts for the absorption efficiency in the critical toxicity study.
 - Aliphatic and Aromatic Petroleum Fractions Due to their makeup of volatile chemicals, all aliphatic carbon ranges, along with aromatics up to EC12, were assigned a GI factor of 0.8. The GI factor for aromatic carbon ranges greater than EC12 to EC34 remained at 0.5 based on the presence of semi-volatile chemicals.



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 Individual Hazardous Substances – The GI factor for 1- and 2methylnaphthalene was changed to 0.89, which is the chemical-specific value for PAHs (see Exhibit 4-1 of RAGS Part E; EPA, 2004). Chemical-specific GI factors were assigned to benzene, toluene, ethylbenzene, and xylenes based on information in ATSDRs toxicological profiles for these chemicals (ATSDR, 2007a; 2007b; 2010, and 2017). MTBE was assigned a GI factor 0.8 because it's volatile.



Acronym List

ABS	Dermal abcorntion fraction
ATSDR	Dermal absorption fraction
	Agency for Toxic Substances and Disease Registry
CLARC	Cleanup Levels and Risk Calculation
CPF	Cancer Potency Factor
CPHEA	Center for Public Health and Environmental Assessment
EC	Equivalent carbon
Ecology	Washington State Department of Ecology
EDB	Ethylene dibromide
EDC	1,2-Dichloroethane
EPA	United States Environmental Protection Agency
GI	Gastrointestinal absorption conversion factor
INH	Groundwater inhalation correction factor
IRIS	Integrated Risk Information System
MTBE	Methyl-tert-butyl-ether
MTCA	Model Toxics Control Act
NCEA	National Center for Environmental Assessment
ORD	Office of Research and Development
ORNL	Oak Ridge National Lab
PAH	Polycyclic Aromatic Hydrocarbon
POG	Project Oversight Group
PPRTV	Provisional Peer-Reviewed Toxicity Value
RAGS	Risk Assessment Guidance for Superfund
RAIS	Risk Assessment Information System
RfD	Reference dose for noncancer effects
RSL	Regional Screening Level
STSC	Superfund Health Risk Technical Support Center
ТРН	Total petroleum hydrocarbon
VPH	Volatile Petroleum Hydrocarbon
WDOH	Washington State Department of Health

References

ATSDR (Agency for Toxic Substances and Disease Registry), 2007a. *Toxicological Profile for Benzene*. U.S. Department of Health and Human Services. August 2007.

ATSDR, 2007b. *Toxicological Profile for Xylene*. U.S. Department of Health and Human Services. August 2007.

ATSDR, 2010. *Toxicological Profile for Ethylbenzene*. U.S. Department of Health and Human Services. November 2010.

ATSDR, 2017. *Toxicological Profile for Toluene*. U.S. Department of Health and Human Services. June 2017

Page 7 of 8 CLARC on Ecology's website: <u>https://ecology.wa.gov/Regulations-Permits/Guidance-technical-assistance/Contamination-clean-up-tools/CLARC</u>



EPA (U.S. Environmental Protection Agency), 2003. *Toxicological Review of Cyclohexane. In Support of Summary Information on the Integrated Risk Information System (IRIS)*. EPA 635/R-03/008. August 2003.

EPA, 2004. *Risk Assessment Guidance for Superfund, Vol. I: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment)*. Final. July 2004. EPA/540/R/99/005.

EPA, 2009. *Provisional Peer-Reviewed Toxicity Values (PPRTV) for Complex Mixtures of Aliphatic and Aromatic Hydrocarbons (CASRN Various)*. EPA/690/R-09/012F. September 30, 2009.

EPA, 2011. *Provisional Peer-Reviewed Toxicity Values (PPRTV) for 1,1-Biphenyl (CASRN 92-52-4).* EPA/690/R-11/011F. April 4, 2011.

EPA, 2015. OSWER Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air. OSWER Publication 9200.2-154. June 2015

EPA, 2021. Regional Screening Levels for Chemical Contaminants at Superfund Sites. (June 11, 2021).

IRIS (Integrated Risk Information System), 2021. U.S. EPA on-line database (<u>http://www.epa.gov/iris/</u>).

TABLES

	Та	ble 1							
Updated Noncancer Reference Do	ses For Total Petroleum Hydrocarb	on (TPH) Fractions and I	ndividua	al Hazardous Substances R	elated to TPH				
- Revised June 2021									
Equivalent Carbon (EC) Chain Length For TPH Fraction	Toxicity Surrogate Descriptive Of The TPH Fraction Oral RfD (mg/k		Ref.	Inhalation RfD (mg/kg- day) <mark>(1)</mark>	Ref.				
Aliphatic TPH Fractions	-								
Aliphatic EC > 5 to EC 6	Cyclohexane (2)	<u>NTV</u>	(4)	1.71E+00	(a), (b)				
Aliphatic > EC 6 to EC 8	Cyclohexane (2)	<u>NTV</u>	(4)	1.71E+00	(a) <i>,</i> (b)				
Aliphatic > EC 8 to EC 10	See footnote (3)	<u>1.0E-02</u>	(c)	2.86E-02	(c)				
Aliphatic > EC 10 to EC 12	See footnote (3)	<u>1.0E-02</u>	(c)	2.86E-02	(c)				
Aliphatic > EC 12 to EC 16	See footnote (3)	<u>1.0E-02</u>	(c)	2.86E-02	(c)				
Aliphatic > EC 16 to EC 21	White Mineral Oil	<u>3.0E+00</u>	(c)	NTV	(c)				
Aliphatic > EC 21 to EC 34	White Mineral Oil	<u>3.0E+00</u>	(c)	NTV	(c)				
Aromatic TPH Fractions									
	BTEX Compounds, Toxicity	See individual BTEX		See individual BTEX					
Aromatic EC > 5 to EC 8	Assessed Individually	chemicals below		chemicals below	(a)				
Aromatic > EC 8 to EC 10	Isopropyl benzene (Cumene)	1.0E-01	(a)	1.14E-01	(a)				
Aromatic > EC 10 to EC 12	Naphthalene	2.0E-02	(a)	8.57E-04	(a)				
Aromatic > EC 12 to EC 16	1,1 - Biphenyl	<u>5.0E-01</u>	(a)	<u>1.14E-04</u>	(d)				
Aromatic > EC 16 to EC 21	Pyrene	3.0E-02	(a)	NTV					
Aromatic > EC 21 to EC34	Fluoranthene	4.0E-02	(a)	NTV					

	Та	ble 1								
Updated Noncancer Reference Do	oses For Total Petroleum Hydrocarb	on (TPH) Fractions and	Individua	al Hazardous Substances F	Related to TPH					
- Revised June 2021										
Individual Hazardous Substances										
Chemical	Toxicity Surrogate Descriptive Of The TPH Fraction	Oral RfD (mg/kg-day)	Ref.	Inhalation RfD (mg/kg- day)	Ref.					
Benzene	No Surrogate Necessary	4.0E-03	(a)	8.57E-03	(a)					
Toluene	No Surrogate Necessary	8.0E-02	(a)	1.43E+00	(a)					
Ethylbenzene	No Surrogate Necessary	1.0E-01	(a)	2.86E-01	(a)					
Xylene(s)	No Surrogate Necessary	2.0E-01	(a)	2.86E-02	(a)					
Naphthalene	No Surrogate Necessary	2.0E-02	(a)	8.57E-04	(a)					
1-methylnaphthalene	No Surrogate Necessary	<u>7.0E-02</u>	(e)	<u>NTV</u>						
2-methylnaphthalene	No Surrogate Necessary	4.0E-03	(a)	<u>NTV</u>						
n-hexane (2)	No Surrogate Necessary	6.0E-02	(f)	2.00E-01	(a)					
Methyl-tert-butyl-ether (MTBE)	No Surrogate Necessary	NTV		8.57E-01	(a)					
Ethylene Dibromide (EDB)	No Surrogate Necessary	9.0E-03	(a)	2.57E-03	(a)					
1,2-Dichloroethane (EDC)	No Surrogate Necessary	<u>6.0E-03</u>	(g)	<u>2.00E-03</u>	(g)					
Benzo(a)pyrene	No Surrogate Necessary	<u>3.0E-04</u>	(a)	<u>5.71E-07</u>	(a)					

Notes:

Updated values are bold and underlined

(1) Derivation of inhalation RfDs from inhalation reference concentrations (RfCs) are based on the following: RfDi mg/(kg-day) = RfC (mg/m³) × $20 \text{ m}^3/\text{day} \div 70 \text{ kg}$, where $20 \text{ m}^3/\text{day}$ is the assumed adult inhalation rate, and 70 kg is the assumed adult body weight.

(2) Cyclohexane is used as the surrogate for these fractions because n-hexane's contribution to overall toxicity is separately evaluated using its own RfD. Testing for n-hexane is required when volatile petroleum hydrocarbon (VPH) analysis is performed for Method B or C (*see* MTCA Rule Table 830-1, Footnote 9).

(3) EPA's 2009 PPRTV for midrange aliphatic hydrocarbon streams (EC>8-EC16) (EPA, 2009).

(4) EPA has concluded that available information is not adequate for a route-to-route extrapolation from the inhalation pathway to the oral pathway for this chemical (IRIS, 2021; EPA, 2003).

Updated Noncancer Reference Doses For Total Petroleum Hydrocarbon (TPH) Fractions and Individual Hazardous Substances Related to TPH - Revised June 2021

Acronyms (undefined in the Table):

BTEX = Benzene, Toluene, Ethylbenzene, Xylene(s); IRIS = Integrated Risk Information System; NTV = No Toxicity Value Available; PPRTV = Provisional Peer-Reviewed Toxicity Value; RfD = Reference Dose

References:

(a) IRIS, 2021. U.S. EPA on-line database (http://www.epa.gov/iris/).

(b) EPA, 2003. Toxicological Review of Cyclohexane. In Support of Summary Information on the Integrated Risk Information System (IRIS). EPA 635/R-03/008. August 2003.

(c) EPA, 2009. Provisional Peer-Reviewed Toxicity Values (PPRTV) for Complex Mixtures of Aliphatic and Aromatic Hydrocarbons (CASRN Various). EPA/690/R-09/012F. September 30, 2009.

(d) EPA, 2011. Provisional Peer-Reviewed Toxicity Values (PPRTV) for 1,1-Biphenyl (CASRN 92-52-4). EPA/690/R-11/011F. April 4, 2011.

(e) ATSDR, 2005. Toxicological Profile for Naphthalene, 1-Methylnaphthalene, and 2-Methylnaphthalene. U.S. Department of Health and Human Services. Public health Service. Agency for Toxic Substances and Disease Registry. August 2005.

(f) EPA, 1997. Health Effects Assessment Summary Tables . FY 1997 Update. EPA-540-R-97-036. July 1997.

(g) EPA, 2010. Provisional Peer-Reviewed Toxicity Values (PPRTV) for 1,2-Dichloroethane (CASRN 107-06-2). EPA/690/R-10/011F. October 1, 2010.

Table 2									
Updated Cancer Potency Factors (CPFs) For Individual Hazardous Substances Related to Total									
Petroleum Hydrocarbons (TPH) - Revised June 2021**									
	Oral CPF (kg-		Inhalation CPF (kg-						
Chemical	day/mg)	Source	day/mg) <mark>(1)</mark>	Source					
Benzene	5.5E-02	I	2.73E-02	I					
Naphthalene	NTV		<u>1.19E-01</u>	С					
1-methylnaphthalene	<u>2.9E-02</u>	Р	NTV						
Methyl-tert-butyl-ether (MTBE)	<u>1.80E-03</u>	С	<u>9.10E-04</u>	С					
Ethylene Dibromide (EDB)	<u>2.0E+00</u>	I	<u>2.10E+00</u>	I					
1,2-Dichloroethane (EDC)	9.1E-02	I	9.10E-02	I					
Benzo(a)anthracene	<u>1.0E-01</u>	(2)	<u>2.10E-01</u>	(2)					
Benzo(b)fluoranthene	<u>1.0E-01</u>	(2)	<u>2.10E-01</u>	(2)					
Benzo(k)fluoranthene	<u>1.0E-01</u>	(2)	<u>2.10E-01</u>	(2)					
Benzo(a)pyrene	<u>1.0E+00</u>	I	<u>2.10E+00</u>	I					
Chrysene	<u>1.0E-02</u>	(2)	<u>2.10E-02</u>	(2)					
Dibenz(a,h)anthracene	<u>1.0E-01</u>	(2)	<u>2.10E-01</u>	(2)					
Indeno(1,2,3-cd)pyrene	<u>1.0E-01</u>	(2)	<u>2.10E-01</u>	(2)					

Notes:

Updated values are bold and underlined

(1) Derivation of inhalation CPFs (CPFi) from inhalation unit risks (URFs) are based on the following: CPFi kg-day/mg = [URF (m^3/ug) × 70 kg] ÷ [20 $m^3/day \times 0.001$ mg/ug], where 20 m^3/day is the assumed adult inhalation rate, and 70 kg is the assumed adult body weight.

(2) Derived using Toxicity Equivalent Factors per Ecology Implementation Memo 10 (Ecology, 2015). ** Individual petroleum related hazardous substances with CPFs only, or CPFs in addition to reference doses, are evaluated independently for purposes of estimating cancer risks and calculating cleanup levels. Aliphatic and aromatic TPH fractions are evaluated based only on their noncancer additive effects.

Acronyms (undefined in the Table):

NTV = No Toxicity Value Available

Sources:

C = Cal EPA (California Environmental Protection Agency)

I = IRIS (Integrated Risk Information System) online database from the Environmental Protection Agency (EPA). http://www.epa.gov/iris/

P = PPRTV - Provisional Peer-Reviewed Toxicity Values from EPA's Superfund Health Risk Technical Support Center (STSC) (STSC is within EPA's Office of Research and Development's (ORD's) Center for Public Health and Environmental Assessment, formerly known as the National Center for Environmental Assessment [NCEA]).

Ecology, 2015. Evaluating the Human Health Toxicity of Carcinogenic PAHs (cPAHs) Using Toxicity Equivalency Factors (TEFs). Impletation Memorandum 10. April 20, 2015.

Updated Physical/Chemical and Exposure Parameters For Total Petroleum Hydrocarbon (TPH) Fractions and Individual Hazardous Substances Related to TPH - Revised August 2022

Fuel Fraction		Physical/Chemical Properties (1)					Exposure Parameters		
Equivalent Carbon (EC) Chain Length For TPH Fraction	Molecular Weight MW (g/mol)	Solubility S mg/L	Hcc (2) (Henry's Law Constant) (unitless)	Koc (Soil Organic Carbon-Water Partitioning Coefficient) (L/kg)	Liquid Density (mg/L)	INH <mark>(3)</mark> (Ground Water Inhalation Correction Factor) (unitless)	ABS (4) Dermal Absorption Fraction (unitless)	GI (5) Gastrointestinal Absorption Conversion Factor (unitless)	
Aliphatic TPH Fractions									
Aliphatic EC > 5 to EC 6	81	3.60E+01	3.30E+01	8.00E+02	6.70E+05	2	0.03	0.8	
Aliphatic >EC 6 to EC 8	100	5.40E+00	5.00E+01	3.80E+03	7.00E+05	2	0.03	0.8	
Aliphatic > EC 8 to EC 10	130	4.30E-01	8.00E+01	3.02E+04	7.30E+05	2	0.03	0.8	
Aliphatic > EC 10 to EC 12	160	3.40E-02	1.20E+02	2.34E+05	7.50E+05	2	0.03	0.8	
Aliphatic > EC 12 to EC 16	200	7.60E-04	5.20E+02	5.37E+06	7.70E+05	<u>2</u>	<u>0.03</u>	<u>0.8</u>	
Aliphatic > EC 16 to EC 21	270	1.30E-06	4.90E+03	9.55E+09	7.80E+05	<u>2</u>	<u>0.03</u>	<u>0.8</u>	
Aliphatic > EC 21 to EC 34	400	1.50E-11	1.00E+05	1.07E+10	7.90E+05	<u>2</u>	<u>0.03</u>	<u>0.8</u>	
Aromatic TPH Fractions									
Aromatic EC > 5 to EC 8			_	See individual BTEX cl	hemicals below			_	
Aromatic > EC 8 to EC 10	120	6.50E+01	4.80E-01	1.58E+03	8.70E+05	2	0.03	0.8	
Aromatic > EC 10 to EC 12	130	2.50E+01	1.40E-01	2.51E+03	9.00E+05	2	0.03	0.8	
Aromatic > EC 12 to EC 16	150	5.80E+00	5.30E-02	5.01E+03	1.00E+06	<u>2</u>	0.1	0.5	
Aromatic > EC 16 to EC 21	190	5.10E-01	1.30E-02	1.58E+04	1.16E+06	<u>2</u>	0.1	0.5	
Aromatic > EC 21 to EC34	240	6.60E-03	6.70E-04	1.26E+05	1.30E+06	1	0.1	0.5	

Updated Physical/Chemical and Exposure Parameters For Total Petroleum Hydrocarbon (TPH) Fractions and Individual Hazardous Substances Related to TPH - Revised August 2022

Chemical	Physical/Chemical Properties					Exposure Parameters			
Chemical	Molecular Weight MW (g/mol)	Solubility S mg/L	Hcc (6) (Henry's Law Constant) 13 degrees C (unitless)	Koc (Soil Organic Carbon-Water Partitioning Coefficient) (L/kg)	Liquid Density (mg/L)	INH (Ground Water Inhalation Correction Factor) (unitless)	ABS Dermal Absorption Fraction (unitless)	GI Gastrointestinal Absorption Conversion Factor (unitless)	
Benzene	78	1.75E+03	<u>1.34E-01</u>	6.20E+01	8.77E+05	2	0.0005	<u>0.97</u>	
Toluene	92	5.26E+02	<u>1.49E-01</u>	1.40E+02	8.67E+05	2	0.03	1	
Ethylbenzene	106	1.69E+02	<u>1.64E-01</u>	2.04E+02	8.67E+05	2	0.03	0.92	
Xylene(s)	106	1.71E+02	<u>1.41E-01</u>	2.33E+02	8.75E+05	2	0.03	<u>0.92</u>	
Naphthalene	128	3.10E+01	<u>8.28E-03</u>	1.19E+03	1.15E+06	2	0.13	0.89	
1-methylnaphthalene	142.2	<u>2.58E+01</u>	<u>6.32E-03</u>	<u>2.53E+03</u>	<u>1.02E+06</u>	2	<u>0.13</u>	<u>0.89</u>	
2-methylnaphthalene	142.2	2.46E+01	<u>7.00E-03</u>	<u>2.48E+03</u>	<u>1.01E+06</u>	2	<u>0.13</u>	<u>0.89</u>	
n-hexane	86	9.50E+00	<u>4.47E+01</u>	3.41E+03	6.59E+05	2	<u>0.0005</u>	0.8	
Methyl-tert-butyl-ether (MTBE)	88	5.00E+04	<u>1.12E-02</u>	1.09E+01	7.44E+05	2	<u>0.0005</u>	<u>0.8</u>	
Ethylene Dibromide (EDB)	<u>187.86</u>	<u>3.91E+03</u>	<u>1.41E-02</u>	6.60E+01	<u>2.17E+06</u>	2	0.03	0.8	
1,2-Dichloroethane (EDC)	<u>98.96</u>	<u>8.60E+03</u>	<u>2.76E-02</u>	3.80E+01	<u>1.25E+06</u>	2	0.03	0.8	
Benzo(a)anthracene	228.3	9.40E-03	<u>9.60E-05</u>	3.58E+05	1.27E+06	1	0.13	0.89	
Benzo(b)fluoranthene	<u>252.32</u>	1.50E-03	<u>6.04E-06</u>	<u>5.99E+05</u>	1.30E+06	1	0.13	0.89	
Benzo(k)fluoranthene	<u>252.32</u>	8.00E-04	<u>4.28E-06</u>	<u>5.87E+05</u>	1.30E+06	1	0.13	0.89	
Benzo(a)pyrene	<u>252.32</u>	1.62E-03	<u>3.61E-06</u>	9.69E+05	<u>1.35E+06</u>	1	0.13	0.89	
Chrysene	228.3	<u>2.00E-03</u>	<u>3.87E-05</u>	<u>1.81E+05</u>	1.27E+06	1	0.13	0.89	
Dibenz(a,h)anthracene	<u>278.36</u>	2.49E-03	<u>7.45E-07</u>	1.79E+06	<u>1.28E+06</u>	1	0.13	0.89	
Indeno(1,2,3-cd)pyrene	<u>276.34</u>	<u>1.90E-04</u>	<u>2.09E-06</u>	<u>1.95E+06</u>	<u>1.40E+06</u>	1	0.13	0.89	

Notes:

Updated values are bold and underlined

(1) Physical/Chemical parameters listed in the MTCA Rule (Tables 747-1 and 747-4) were used where available. Otherwise, parameter values from the Oak Ridge National Lab (ORNL) Risk Assessment Information System (RAIS) chemical database were used. Physical/Chemical data in CLARC (except those listed in the MTCA Rule) have been updated to reflect values from the ORNL RAIS chemical database.

(2) Henry's law for the petroleum fractions were taken from MTCA Table 747-4. The values were not adjusted to 13° Celsius as they are approximations that represent a range of chemicals. Also, other physical/chemical specific data needed to make the adjustment (e.g., critical temperature, boiling point) specific for these fractions have not been identified.

(3) The INH factor was updated for several petroleum carbon fractions including benzo(a) anthracene (changed from 1 to 2) to reflect their vapor forming potential based on their Henry's law being greater the 1×10^{-5} atm-m³/mol.

(4) In the absence of a chemical-specific dermal ABS value, MTCA defaults were applied in accordance with WAC 173-340-740(3)(c)(iii). An ABS of 13% was used for polycyclic aromatic hydrocarbons (PAHs) (EPA, 2004).

Updated Physical/Chemical and Exposure Parameters For Total Petroleum Hydrocarbon (TPH) Fractions and Individual Hazardous Substances Related to TPH - Revised August 2022

(5) In the absence of a chemical-specific dermal GI conversion factor, MTCA defaults were applied in accordance with WAC 173-340-740(3)(c)(iii). A GI factor of 0.89 was used for PAHs (EPA, 2004). Chemical-specific GI factors were assigned to benzene, ethylbenzene, toluene, and xylenes based on information in ATSDRs toxicological profiles for these chemicals (ATSDR, 2007a; 2007b; 2010, and 2017).

(6) Consistent with CLARC, data from ORNL RAIS (i.e., boiling point, critical temperature, enthalpy of vaporization), along with formulas in EPA's Vapor Intrusion Screening Level (VISL) excel spreadsheet system (Chem Props worksheet), were used to adjust Henry's law based on 25° Celsius to 13° Celsius for the individual chemicals.

Acronyms:

MTCA = Model Toxics Control Act; NTV = No Toxicity Value Available; BTEX = Benzene, Toluene, Ethylbenzene, Xylenes; RAG = Risk Assessment Guidance for Superfund; SVOC = Semi-volatile organic chemical

Table 4. Model Toxics Control Act (MTCA) TPH Excel Workbook Tool (Ver. 11.1) – Updated Chemical Database – Revised August 2022

	Physical-Chemical Properties									
	1	2	3	4	5	6	7			
CAS NO	Compound or Petroleum Equivalent Carbon Fraction	Equivalent Carbon Number	rbon Weight	Aqueous Solubility	Henry's Law Constant	Soil Organic Carbon-Water Partitioning Coef	Liquid Density			
			GFW	S	H _{cc}	K _{oc}	ρ			
			mg/mol	mg/L	unitless	L/kg	mg/L			
	Petroleum EC Fraction									
	AL_EC >5-6	5.5	8.10E+04	3.60E+01	3.30E+01	8.00E+02	6.70E+05			
	AL_EC >6-8	7	1.00E+05	5.40E+00	5.00E+01	3.80E+03	7.00E+05			
	AL_EC >8-10	9	1.30E+05	4.30E-01	8.00E+01	3.02E+04	7.30E+05			
	AL_EC >10-12	11	1.60E+05	3.40E-02	1.20E+02	2.34E+05	7.50E+05			
	AL_EC >12-16	14	2.00E+05	7.60E-04	5.20E+02	5.37E+06	7.70E+05			
	AL_EC >16-21	19	2.70E+05	1.30E-06	4.90E+03	9.55E+09	7.80E+05			
	AL_EC >21-34	28	4.00E+05	1.50E-11	1.00E+05	1.07E+10	7.90E+05			
	AR_EC >8-10	9	1.20E+05	6.50E+01	4.80E-01	1.58E+03	8.70E+05			
	AR_EC >10-12	10	1.30E+05	2.50E+01	1.40E-01	2.51E+03	9.00E+05			
	AR_EC >12-16	14	1.50E+05	5.80E+00	5.30E-02	5.01E+03	1.00E+06			
	AR_EC >16-21	19	1.90E+05	5.10E-01	1.30E-02	1.58E+04	1.16E+06			
	AR_EC >21-34	28	2.40E+05	6.60E-03	6.70E-04	1.26E+05	1.30E+06			
71-43-2	Benzene	6.5	7.80E+04	1.75E+03	1.34E-01	6.20E+01	8.77E+05			
108-88-3	Toluene	7.6	9.20E+04	5.26E+02	1.49E-01	1.40E+02	8.67E+05			
100-41-4	Ethylbenzene	8.5	1.06E+05	1.69E+02	1.64E-01	2.04E+02	8.67E+05			
	Total Xylenes	8.67	1.06E+05	1.71E+02	1.41E-01	2.33E+02	8.75E+05			
91-20-3	Naphthalene	11.69	1.28E+05	3.10E+01	8.28E-03	1.19E+03	1.15E+06			
90-12-0	1-Methyl Naphthalene		1.42E+05	2.58E+01	6.32E-03	2.53E+03	1.02E+06			
91-57-6	2-Methyl Naphthalene		1.42E+05	2.46E+01	7.00E-03	2.48E+03	1.01E+06			
110-54-3	n-Hexane	6	8.60E+04	9.50E+00	4.47E+01	3.41E+03	6.59E+05			
1634-04-4	MTBE		8.80E+04	5.00E+04	1.12E-02	1.09E+01	7.44E+05			
106-93-4	Ethylene Dibromide (EDB)		1.88E+05	3.91E+03	1.41E-02	6.60E+01	2.17E+06			
107-06-2	1,2 Dichloroethane (EDC)		9.90E+04	8.60E+03	2.76E-02	3.80E+01	1.25E+06			
56-55-3	Benzo(a)anthracene		2.28E+05	9.40E-03	9.60E-05	3.58E+05	1.27E+06			
205-99-2	Benzo(b)fluoranthene		2.52E+05	1.50E-03	6.04E-06	5.99E+05	1.30E+06			
207-08-9	Benzo(k)fluoranthene		2.52E+05	8.00E-04	4.28E-06	5.87E+05	1.30E+06			
50-32-8	Benzo(a)pyrene		2.52E+05	1.62E-03	3.61E-06	9.69E+05	1.35E+06			
218-01-9	Chrysene		2.28E+05	2.00E-03	3.87E-05	1.81E+05	1.27E+06			
57-70-3	Dibenz(a,h)anthracene		2.78E+05	2.49E-03	7.45E-07	1.79E+06	1.28E+06			
193-39-5	Indeno(1,2,3-cd)pyrene		2.76E+05	1.90E-04	2.09E-06	1.95E+06	1.40E+06			

Table 4. Model Toxics Control Act (MTCA) TPH Excel Workbook Tool (Ver. 11.1) – Updated Chemical Database – Revised August 2022

			Toxicological Properties							
	1	8	9	10	12	13	14	15		
CAS NO	Compound or Petroleum Equivalent Carbon Fraction	Oral Reference Dose	Inhalation Correction Factor	Inhalation Reference Dose	Dermal Absorption Fraction	Gastrointestinal Absorption Conversion Factor	Oral Carcinogenic Potency Factor (with CalEPA's TEF for cPAHs)	Inhalation Carcinogenic Potency Factor (with CalEPA's TEF for cPAHs)		
		RfD _o	INH	RfD _i	ABS _d	GI	CPF _o	CPF _i		
		mg/kg-day	unitless	mg/kg-day	unitless	unitless	kg-day/mg	kg-day/mg		
	Petroleum EC Fraction									
	AL_EC >5-6	NTV	2	1.71E+00	0.03	0.8				
	AL_EC >6-8	NTV	2	1.71E+00	0.03	0.8				
	AL_EC >8-10	1.00E-02 ↓ 3x	2	2.86E-02 ↓ 3x	0.03	0.8				
	AL_EC >10-12	1.00E-02 ↓ 3x	2	2.86E-02 ↓ 3x	0.03	0.8				
	AL_EC >12-16	1.00E-02 ↓ 3x	2	2.86E-02 ↓ 3x	0.03	0.8				
	AL_EC >16-21	3.00E+00 ↑ 1.5x	2		0.03	0.8				
	AL_EC >21-34	3.00E+00 ↑ 1.5x	2		0.03	0.8				
	AR_EC >8-10	1.00E-01	2	1.14E-01	0.03	0.8				
	AR_EC >10-12	2.00E-02	2	8.57E-04	0.03	0.8				
	AR_EC >12-16	5.00E-01 1 0x	2	1.14E-04 ↓ 430 x	0.1	0.5				
	AR_EC >16-21	3.00E-02	2		0.1	0.5				
	AR_EC >21-34	4.00E-02	1		0.1	0.5				
71-43-2	Benzene	4.00E-03	2	8.57E-03	0.0005	0.97	5.50E-02	2.73E-02		
108-88-3	Toluene	8.00E-02	2	1.43E+00	0.03	1				
100-41-4	Ethylbenzene	1.00E-01	2	2.86E-01	0.03	0.92				
	Total Xylenes	2.00E-01	2	2.86E-02	0.03	0.92				
91-20-3	Naphthalene	2.00E-02	2	8.57E-04	0.13	0.89		1.19E-01		
90-12-0	1-Methyl Naphthalene	7.00E-02 ↑ 1.4x	2	NTV	0.13	0.89	2.90E-02			
91-57-6	2-Methyl Naphthalene	4.00E-03	2	NTV	0.13	0.89				
110-54-3	n-Hexane	6.00E-02	2	2.00E-01	0.0005	0.8				
1634-04-4	MTBE		2	8.57E-01	0.0005	0.8	1.80E-03	9.10E-04		
106-93-4	Ethylene Dibromide (EDB)	9.00E-03	2	2.57E-03	0.03	0.8	$2.00E+00 \downarrow 42.5x$	2.10E+00 ↑ 2.7x		
107-06-2	1,2 Dichloroethane (EDC)	6.00E-03 ↓ 5x	2	2.00E-03 ↑ 1.4x	0.03	0.8	9.10E-02	9.10E-02		
56-55-3	Benzo(a)anthracene		1		0.13	0.89	1.00E-01 ↓ 7.3x	2.10E-01 ↓ 2.9 x		
205-99-2	Benzo(b)fluoranthene		1		0.13	0.89	1.00E-01 ↓ 7.3x	2.10E-01 ↓ 2.9 x		
207-08-9	Benzo(k)fluoranthene		1		0.13	0.89	1.00E-01 ↓ 7.3x	2.10E-01 ↓ 2.9 x		
50-32-8	Benzo(a)pyrene	3.00E-04	1	5.71E-07	0.13	0.89	1.00E+00 ↓ 7.3x	$2.10E+00 \downarrow 2.9x$		
	Chrysene		1		0.13	0.89	1.00E-02 ↓ 7.3x	2.10E-02 ↓ 2.9 x		
57-70-3	Dibenz(a,h)anthracene		1		0.13	0.89	1.00E-01 ↓ 7.3x	2.10E-01 ↓ 2.9 x		
	Indeno(1,2,3-cd)pyrene		1		0.13	0.89	1.00E-01 ↓ 7.3x	2.10E-01 ↓ 2.9 x		

Notes (updates are in blue font):

NTV = Current values in the MTCA TPH spreadsheet are removed due to "No toxicity value available".

 \downarrow = Noncancer - The reference dose decreased which results in lower noncancer-based cleanup levels; Cancer - The cancer potency factor decreased which results in an increase in cancer-based cleanup levels. The magnitude of decrease is noted.

 \uparrow = Noncancer - The reference dose increased which results in an increase in noncancer-based cleanup levels; Cancer - The cancer potency factor increased which results in a decrease in cancer-based cleanup levels. The magnitude of increase is noted.

Toxicity changes with no arrow designation = The current MTCA TPH database had no toxicity critieria identified for the chemical. New available toxicity criteria has been added.

ATTACHMENT 1

Calculation of Method B and Method C Cleanup Levels For Petroleum Mixtures



Introduction

Cleanup levels for Total Petroleum Hydrocarbon (TPH) mixtures are determined using the fractionated analytical approach. This approach divides the petroleum mixture into equivalent hydrocarbon numbers. Use of the fractionated approach requires the determination of the composition of the petroleum mixture.

Cleanup levels for petroleum mixtures are dependent on the composition of the mixture.

Method A cleanup levels for petroleum mixtures provided in Table 720-1 (Method A Ground Water Cleanup Levels), Table 740-1 (Method A Soil Cleanup Levels for Unrestricted Land Use) and Table 745-1 (Method A Soil Cleanup Levels for Industrial Land Use) are based on **assumed compositions**.

Method B and Method C cleanup levels for petroleum mixtures are based on **site-specific compositions**. Identifying the composition requires a site-specific analysis of either the contaminated medium or the source of the contamination (either the product released or another contaminated medium). See Table 830-1 for a list of contaminants to test for when establishing cleanup levels for petroleum mixtures.

Because cleanup levels for petroleum mixtures are dependent of the composition of the mixture and because the composition must be determined on a site-specific basis, **CLARC does not provide pre-calculated standard Method B or C formula values for petroleum mixtures**.

To calculate soil and ground water cleanup levels for petroleum mixtures, the assessor should use the Workbook and associated User's Guide (Publication No. 01-09-073) provided by the Department of Ecology.

Establishing Cleanup Levels for Petroleum Mixtures

Ground Water

Cleanup levels must be established for the total petroleum hydrocarbon (TPH) mixture as a whole, as well as for individual hazardous substances (TPH components) within the mixture, such as benzene, ethylbenzene, toluene, and xylene.

Under Method B and Method C, the cleanup levels for individual TPH components are established just like they would be for any other hazardous substance.

To establish a site-specific TPH cleanup level under Method B or Method C, the composition of the petroleum mixture in the ground water must be determined. Determining the composition requires the analysis of either the ground water or the source of the contamination (the product itself or contaminated soil) for petroleum fractions and other toxic components likely to be present. See Table 830-1 for a list of contaminants to test for when establishing cleanup levels for petroleum mixtures. If the analysis is based on the product or contaminated soil composition, a ground water composition must be predicted using a fate and transport model under WAC 173-340-747, such as the 3-phase or 4-phase model.

The actual or predicted ground water composition is used in Equation 720-3 to calculate a total petroleum hydrocarbon (TPH) cleanup level that takes into account the combined noncarcinogenic effects of the petroleum mixture. This TPH cleanup level may need to be adjusted downward to take into account the cleanup levels for individual petroleum components. A further adjustment may be necessary if modeling or ground water monitoring indicates biological degradation of residual petroleum would result in violation of the drinking water standards for other chemicals. This is most likely to be a concern for naturally occurring metals such as arsenic, iron and manganese that can be brought into solution by depletion of oxygen in the ground water during petroleum degradation.

See WAC 173-340-720 (4)(b)(iii)(C) and (5)(b)(iii)(C).

Surface Water

Cleanup levels must be established for the total petroleum hydrocarbon (TPH) mixture as a whole, as well as for individual hazardous substances (TPH components) within the mixture, such as benzene, ethylbenzene, toluene, and xylene.

Under Method B and Method C, cleanup levels for individual TPH components are established just like they would be for any other hazardous substance. To establish a site-specific TPH cleanup level under Method B or Method C, the

composition of the petroleum mixture in the surface water must be determined. Determining the composition requires the analysis of the surface water or the source of the petroleum contamination (the product itself or contaminated soil or ground water) for petroleum fractions and other toxic components likely to be present. See Table 830-1 for a list of contaminants to test for when establishing cleanup levels for petroleum mixtures. If the analysis is based on the source of the contamination, a water phase composition must be predicted using a fate and transport model under WAC 173-340-747, such as the 3-phase or 4-phase model.

The actual or predicted water composition is used in a risk assessment equation to calculate a cleanup level that takes into account the combined human health risk of the petroleum mixture. This equation is not specified in the regulation. However, an acceptable equation may be obtained from Ecology. This cleanup level may need to be adjusted downward to take into account the cleanup levels of the individual petroleum components.

As an alternative to calculating a site-specific TPH cleanup level, the regulation allows for the use of the applicable TPH ground water cleanup levels in Table 720-1. Use of these values would avoid the need to conduct fractionated petroleum analyses.

The cleanup levels for TPH and the TPH components must also be at least as stringent as concentrations that are protective of fish and aquatic life, as well as wildlife, just as for any other hazardous substance. Whole effluent toxicity (WET) testing may be used to demonstrate that a concentration is protective of fish and aquatic life. Other methods may need to be used to demonstrate that a concentration is protection is protective of wildlife, if this is a concern at the site.

See WAC 173-340-730(3)(b)(iii)(C) and (4)(b)(iii)(C).

Soil

Cleanup levels must be established for the total petroleum hydrocarbon (TPH) mixture as a whole, as well as for individual hazardous substances (TPH components) within the mixture, such as benzene, ethylbenzene, toluene, and xylene.

To establish a site-specific TPH cleanup level under Method B or Method C, the composition of the petroleum mixture in the soil must be determined. Determining the composition requires the analysis of either the soil or the product released for petroleum fractions and other toxic components likely to be present. See Table 830-1 for a list of contaminants to test for when establishing cleanup levels for petroleum mixtures.

• **Direct Contact Pathway:** For petroleum mixtures, the regulation requires a concurrent evaluation of ingestion and dermal absorption. The petroleum mixture composition is used in Equation 740-3 (or, if using Method C, Equation 745-3) to calculate a protective concentration for TPH that takes into account the combined noncarcinogenic effects of the petroleum mixture. Protective concentrations for

individual TPH components are established using Equations 740-4 and 740-5 (or, if using Method C, Equations 745-4 and 745-5). The TPH concentration may need to be adjusted downward to take into account the protective concentrations for individual TPH components. See WAC 173-340-740(3)(b)(iii)(B)(III) and 173-340-745(5)(b)(iii)(B)(III).

- **Leaching Pathway:** Protective concentrations for TPH and the TPH components must be established using the methods described in WAC 173-340-747.
- **Vapor Pathway:** Since TPH and TPH components contain volatile organic compounds, the vapor pathway must be evaluated whenever one of the conditions specified in the regulation exists at a site. Protective concentrations may be determined using one or more of the methods described in the regulation.

In addition to accounting for human health impacts, soil cleanup levels for TPH and the TPH components must also account for any potential impacts to terrestrial ecological receptors (plants and animals), just as for any other hazardous substance.

Air

Cleanup levels must be established for the total petroleum hydrocarbon (TPH) mixture as a whole as well as for individual hazardous substances (TPH components) within the mixture, such as benzene, ethylbenzene, toluene, and xylene.

Under Method B and Method C, the cleanup levels for individual TPH components are established just like they would be for any other hazardous substance.

To establish TPH cleanup levels under Method B or Method C, the composition of the petroleum mixture in the air must be determined. Determining the composition requires the analysis of either the air or the source of the contamination (the product itself or contaminated soil or ground water) for petroleum fractions and other toxic components likely to be present. See Table 830-1 for a list of contaminants to test for when establishing cleanup levels for petroleum mixtures. If the analysis is based on the source of the contamination, a soil vapor composition must be predicted using a fate and transport model under WAC 173-340-747, such as the 3-phase or 4phase model.

The actual or predicted air composition is used to calculate a total petroleum hydrocarbon (TPH) cleanup level that takes into account the combined noncarcinogenic effects of the petroleum mixture. This equation is not specified in the regulation. However, an acceptable equation can be obtained from Ecology. This cleanup level may need to be adjusted downward to take into account the cleanup levels of any individual petroleum components.

See WAC 173-340-750(3)(b)(ii)(C) and (4)(b)(ii)(C).

ATTACHMENT 2

• Version 3.1 of CLARC, November 2001

Table – Recommended Reference Doses for Petroleum Fractions and Individual Hazardous Substance

Recommended References Doses for Petroleum Fractions and Individual Hazardous Substances

Fraction/Compound and Equivalent Carbon (EC) ¹	Surrogate	Oral RfD (mg/kg-day)	Inhalation RfD (mg/kg-day)	Source
Aliphatic EC5 to EC6	Cyclohexane	5.7	5.7	EPA
Aliphatic >EC6 to EC8	Cylcohexane	5.7	5.7	EPA
Aliphatic >EC8 to EC10	(see Note 2)	0.03	0.085	EPA
Aliphatic >EC10 to EC12	(see Note 2)	0.03	0.085	EPA
Aliphatic >EC12 to EC16	(see Note 2)	0.03	NA ³	EPA
Aliphatic >EC16 to EC21	Mineral Oil	2	NA ³	CWG/EPA
Aliphatic >EC21 to EC36	Mineral Oil	2	NA ³	CWG/EPA
Aromatic EC8 to EC10	Biphenyl	0.05	0.05	EPA
Aromatic >EC10 to EC12	Biphenyl	0.05	0.05	EPA
Aromatic >EC12 to EC16	Biphenyl	0.05	NA ³	EPA
Aromatic >EC16 to EC21	Pyrene	0.03	NA ³	MaDEP/EPA
Aromatic >EC21 to EC36	Pyrene	0.03	NA ³	MaDEP/EPA
n-Hexane		0.06	0.057	EPA
Benzene		0.003	0.0017	EPA
Ethyl benzene		0.1	0.286	EPA
Toluene		0.2	0.114	EPA
Xylenes		2	0.2	EPA
Naphthalene		0.02	0.00086	EPA
1,2 dibromoethane		0.000057	0.000057	EPA

Footnotes:

- (1) In some cases the EPA fractions are slightly different but for consistency and simplicity they were adjusted to these which are very close (within one equivalent carbon number).
- (2) The aliphatic fractions with an oral reference dose = 0.03 and an inhalation reference dose = 0.085 is based on a "mixture of alkanes" for ingestion and ATSDR chronic MRL (minimal risk level) of 0.3 mg/m3 for JP-7 as the inhalation surrogate for EC8 to EC16 which equals an inhalation RfD of 0.085 mg/kg-day.
- (3) "Volatile" is defined as EC 12 and less plus naphthalenes; therefore no inhalation reference doses are needed for higher fractions.

Abbreviations:

- NA = Not Applicable (because not volatile; see footnote 3)
- CWG = Total Petroleum Hydrocarbon Criteria Working Group
- MaDEP = Massachusetts's Department of Environmental Protection
- EPA = Environmental Protection Agency (reviews of CWG & MaDEP recommendations)

ATTACHMENT 3

- 2005/2006 correspondence between Ecology and EPA Regarding Reference Doses for Petroleum Mixtures
- Table Updated Reference Doses for Total Petroleum Hydrocarbon (TPH) Fractions and Individual Hazardous Substances Related to TPH – Revised January 2006



Supporting material for Cleanup Levels and Risk Calculation (CLARC) Washington State Department of Ecology – Toxics Cleanup Program

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY REGION 10 1200 Sixth Avenue Seattle, Washington 98101

February 14, 2005

Reply to Attn of: OEA-095

Craig M. McCormack, Pharm D. Toxics Cleanup Program Department of Ecology P. O. Box 47600 Olympia, WA 98504-7600

Dear Dr. McCormack:

Thank you for your letter of February 9, 2006, describing the changes to the table "Updated Reference Doses for Total Petroleum Hydrocarbon (TPH) Fractions and Individual Hazardous Substances Related to TPH." The updated table is to be incorporated into Ecology's Cleanup Levels and Risk Calculations under the Model Toxic Control Act regulations

The changes appear to be consistent with our discussions over the past few months. I concur with the changes made to the table and its footnotes and believe they represent appropriate interpretations of information available from the IRIS and HEAST databases and from EPA's National Center for Environmental Assessment, including the Superfund Technical Support Center

Sincerely,

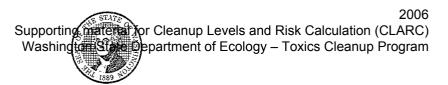
Marcia L.

Marcia L. Bailey, D Env.

cc: Patricia Cirone, Ph D.

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2006



STATE OF WASHINGTON DEPARTMENT OF ECOLOGY

PO Box 47600 • Olympia, WA 98504-7600 • 360-407-6000 TTY 711 or 800-833-6388 (for the speech or hearing impaired)

February 9, 2006

Marcia Bailey, D.Env US EPA Region 10, MS: OEA-095 1200 6th Avenue Seattle, Washington 98101

Dear Dr. Bailey:

The enclosed table, <u>Updated Reference Doses For Total Petroleum Hydrocarbon (TPH)</u> <u>Fractions And Individual Hazar dous Substances Related to TPH – Revised January 2006</u>, consolidates our discussions, e-mails, and overall review of the reference doses appropriate for inclusion in the Department of Ecology's updated TPH table to be incorporated into the Cleanup Levels and Risk Calculations under the Model Toxics Control Act Cleanup Regulation (CLARC). This constitutes an update to the TPH CLARC table that was prepared with your support, in 2004. The information in the updated table will be used by the Department of Ecology's Toxics Cleanup Program to evaluate and develop cleanup levels for dangerous waste sites contaminated with petroleum and selected chemicals that may be associated with petroleum products

The 2006 table recognizes updates that have been made to the EPA Integrated Risk Information System (IRIS) database as of January 2006 and information from EPA's National Center for Environmental Assessment, Superfund Technical Support Center (STSC). For individual hazardous substances, the following changes have been made to the revised January 2006 table:

- 1-Methylnaphthalene has been deleted from the table, because the oral reference dose (RfDo) is no longer supported by STSC. The toxicity of 1-methylnaphthalene in a mixture will now be accounted for by including its measured concentration in the aromatic fraction >EC 10 to EC 12 for both oral and inhalation pathways
- 2-Methylnaphthalene remains in the table with an oral RfD of 0.004 mg/kg-day, supported on IRIS 2- Methylnaphthalene is to be evaluated individually for oral exposure only. There is no inhalation RfD for 2-methylnaphthalene, because STSC does not recommend a route-to-route extrapolation for this chemical The measured concentration of 2-methylnaphthalene should be included in the aromatic >EC 10-12 fraction for purposes of evaluating inhalation exposures.
- Toluene has an oral RfD of 0.08 mg/kg-day and an inhalation RfD of 1.4 mg/kg-day, supported by IRIS.

Supporting material for Cleanup Levels and Risk Calculation (CLARC) Washington State Department of Ecology – Toxics Cleanup Program

2006

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• N-hexane has an oral RfD of 0.06 mg/kg-day and an inhalation RfD of 0.2 mg/kg-day, supported by EPA's Health Effects Assessment Summary Table and IRIS, respectively.

For purposes of documentation, I would appreciate receiving from you, in writing, verification that the information in the enclosed table accurately reflects our mutual understanding and interpretation of the current technical information regarding measures of toxicity for TPH and related hazardous substances.

Thank you for your helpful and continued technical support.

Sincerely, OLUMAD][

Craig R McCormack, Pharm D. Toxics Cleanup Program

Enclosure

Updat	ted Reference Doses For Total Pe	etroleum Hydroca	bon (TPH) Fractions	
	dividual Hazardous Substances	Related to TPH - 1		
Equivalent Carbon (EC)	Toxicity Surrogate	Oral RfD	Inhalation RfD	Documentation
Chain Length For TPH	Descriptive Of The	(mg/kg-day)	(mg/kg-day) (4)	
Fraction	TPH Fraction			
Aliphatic TPH Fractions				
Aliphatic EC 5 to EC 6	Cyclohexane (1)	1.7	1.7	EPA / IRIS
Aliphatic >EC 6 to EC 8	Cyclohexane (1)	1.7	1.7	EPA / IRIS
Aliphatic $>$ EC 8 to EC 10	See footnote (2)	0.03	0.085	(1)
Aliphatic > EC 10 to EC 12	See footnote (2)	0.03	0.085	(1)
Aliphatic > EC 12 to EC 16	See footnote (2)	0.03	0.085	(1)
Aliphatic > EC 16 to EC 21	White Mineral Oil	2	Not Applicable (3)	(4)
Aliphatic > EC 21 to EC 36	White Mineral Oil	2	Not Applicable (3)	(4)
Aromatic TPH Fractions				
Aromatic EC 5 to EC 8	BTEX Compounds, Toxicity	See individual	See individual	EPA / IRIS
	Assessed Individually (5)	chemical below	chemical below	
Aromatic > EC 8 to EC 10	Isopropyl benzene (Cumene)	0.1	0.114	EPA / IRIS
Aromatic > EC 10 to EC 12	Naphthalene	0.02	0.00086	EPA / IRIS
Aromatic > EC 12 to EC 16	1,1 - Biphenyl	0.05	0.05 (6)	EPA / IRIS
Aromatic > EC 16 to EC 21	Pyrene	0.03	Not Applicable (2)	EPA / IRIS
Aromatic > EC 21 to EC36	Fluoranthene	0.04	Not Applicable (2)	EPA / IRIS
	Reference Doses For Individu	al Chemicals Witl	n Noncancer	-
	Toxicities That May B	e Associated with	TPH*	
Chemical	Toxicity Surrogate	Oral RfD	Inhalation RfD	Documentation
	Descriptive Of The TPH Fraction	(mg/kg-day)	(mg/kg-day) (7)	
2- methylnaphthalene	No Surrogate Necessary	0.004	Include in Aromatic > EC 10- EC 12	EPA/IRIS, (8,9)
Benzene	No Surrogate Necessary	0.004	0.00855	EPA/IRIS
Ethylbenzene	No Surrogate Necessary	0.1	0.286	EPA/IRIS
Toluene	No Surrogate Necessary	0.08	1.4	EPA/IRIS
Xylene(s)	No Surrogate Necessary	0.2	0.029	EPA/IRIS
Styrene	No Surrogate Necessary	0.2	0.285	EPA/IRIS
1,2-dibromoethane	No Surrogate Necessary	0.009	0.00257	EPA/IRIS
n-hexane	No Surrogate Necessary	0.06	0.2	EPA/HEAST, IRIS
Methyl-tert-butyl-ether	No Surrogate Necessary	None	0.857	EPA/IRIS

- (1) Where n-hexane is quantitatively analyzed for as an individual chemical, use cyclohexane as the toxicity surrogate for the aliphatic EC 5 to EC 8 fraction, and assess n-hexane based on its own toxicity; if n-hexane is not quantitatively analyzed for as an individual chemical, use n-hexane toxicity as the toxicity surrogate for the entire fraction.
- (2) The Iotal Petroleum Hydrocarbon Criteria Working Group (IPHCWG) and EPA/NCEA PPRIV Derivation Support Document for Iotal Petroleum Hydrocarbons (SRC SF 01-031/10-16-2002). The oral reference dose (RfD) for the aliphatic fractions > EC 8 to EC 16 is based on IPHCWG's analysis of a mixture of alkanes and JP-8 fuel, plus a safety factor of 3 as recommended by NCEA/EPA. The inhalation RfD is based on the AISDR chronic inhalation minimum risk level (MRL), as recommended by NCEA/EPA.
- (3) Not Applicable due to non-volatility
- (4) IPHCWG recommendation based on feeding studies of white mineral oils and EPA/NCEA PPRIV Derivation Support Document for Total Petroleum Hydrocarbons (SRC SF 01-031/10-16-2002).
- (5) BIEX: <u>Benzene</u>; <u>Toluene</u>; <u>Ethylbenzene</u>; <u>Xylene(s)</u>; IRIS: <u>Integrated Risk Information System developed</u> by U.S Environmental Protection Agency
- (6) The inhalation RfD for 1, 1 biphenyl is a direct extrapolation from the oral RfD.
- (7) Derivation of inhalation RfDs from inhalation reference concentrations (RfCs) are based on the following: RfDi mg/(kg-day) = RfC (mg/m³) X 20 m³/ day X 1/ 70 kg, where 20 m3/day is the assumed adult inhalation rate, and 70 kg is the assumed adult body weight

(8) 2-Methylnaphthalene is included in the aromatic >EC 10 to EC 12 fraction when evaluating its hazards from inhalation exposure. 2-Methylnaphthalene does not have an inhalation RfD because STSC does not recommend route to route extrapolation from the oral RfD for this chemical. Use the oral RfD (0.004 mg/kg-day) for 2-methylnaphthalene when evaluating its hazards from the oral route of exposure, and subtract it from the aromatic >EC 10 to EC 12 fraction.

* The information provided in this table is for IPH-related chemicals with reference doses. As has been the case in the past, TPH-related chemicals with cancer potency factors only, or cancer potency factors in addition to reference doses, must be evaluated independently for purposes of estimating risks and calculating cleanup levels. In addition to benzene, these may include the following chemicals, if required to be analyzed, pursuant to Table 830-1 in MTCA: 1,2-dibromoethane, 1,2-dichloroethane, carcinogenic PAHs and PCBs. In addition, lead, which has neither a reference dose nor a cancer potency factor, must be evaluated based on prevention of unacceptable blood lead levels, when it is a potential contaminant at TPH sites.