

User's Guide for MTCATPH Workbook Version 12.0

Workbook Tools for Calculating Soil and Groundwater Cleanup Levels Under the Model Toxics Control Act Cleanup Regulation

Toxics Cleanup Program

Washington State Department of Ecology Olympia, Washington

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Related Publications and Resources

User's Guide for MTCASGL Workbook Version 12.0 - Workbook Tools for Calculating Soil and Groundwater Cleanup Levels under the Model Toxics Control Act Cleanup Regulationsⁱ; Guidance for Remediation of Petroleum Contaminated Sites, Revised June 2016ⁱⁱ; CLARC Guidanceⁱⁱⁱ; Toxicity data and physical/chemical properties for petroleum mixtures^{iv}; Guidance for Silica Gel Cleanup in Washington State^v; Guidance for Evaluating Vapor Intrusion in Washington State: Investigation and Remedial Action^{vi}; Analytical Methods for Petroleum Hydrocarbons^{vii}; Implementation Memo #10^{viii}; Implementation Memo # 23^{ix}

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Acronyms and Abbreviations

Acronym or	Definition
abbreviation	Deminion
°C	Degrees Celsius
μg/L	micrograms per liter for ground water media sample (same as parts per
μ9/Ε	billion ppb)
1 x 10 ⁻⁵ or 1E-	One excess cancer case in a population of one hundred thousand
05 Cancer Risk	individuals
1 x 10 ⁻⁶ or 1E-	One excess cancer case in a population of one million individuals
06 Cancer Risk	One excess cancer case in a population of one million individuals
	TPH concentration at which air-filled pore volume is completely filled by
100% NAPL	equilibrated NAPL. This concentration is usually well above Residual
	Saturation Level
AB1	Gastrointestinal absorption fraction
ABS _d	Dermal absorption fraction
ABS _i	Inhalation absorption fraction
ADAF	Age-Dependent Adjustment Factors
AF	Adherence factor
AL	Aliphatic
AL_EC	Aliphatic Equivalent Carbon Number
AR	Aromatic
AR_EC	Aromatic Equivalent Carbon Number
ARAR	Applicable, Relevant, and Appropriate Requirements
atm	Atmosphere
BaP	Benzo(a)pyrene
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
	Ecology, Cleanup Levels and Risk Calculations under the Model Toxics
CLARC	Control Act Cleanup Regulation; Refer to Ecology's interactive web site at
	https://ecology.wa.gov/clarc
сРАН	Carcinogenic Polycyclic Aromatic Hydrocarbon
CPF	Cancer potency factor
C _{sat}	Soil saturation limit
CUL	Cleanup level
DF	Dilution factor
EC	Equivalent Carbon number
Ecology	Washington State Department of Ecology
ELE	Early-life exposure
EPA	U.S. Environmental Protection Agency
EPH	Extractable petroleum hydrocarbons
foc	Fraction soil organic carbon
foc	Soil fraction of organic carbon
GI	Gastrointestinal absorption conversion factor

Acronym or abbreviation	Definition	
H _{cc}	Henry's law (dimensionless form)	
Hg	Mercury	
HI	Hazard Index	
HQ	Hazard Quotient	
INH	Inhalation correction factor	
IRIS	Integrated Risk Information System Database	
K	Kelvin	
K _{oc}	Soil Organic Carbon-Water Partitioning Coefficient	
kPA	kilopascal	
L/kg	Liters per kilogram	
MCL	Maximum Contaminant Level	
MDL	Method Detection Limit	
mg/kg	milligrams per kilogram for soil media sample (same as part per million: ppm)	
mg/L	milligrams of contaminant per liter of water	
mm	millimeter	
MTCA	Model Toxics Control Act	
MTCASGL 12.0	The Excel Workbook Version 12.0 for calculating Soil and Groundwater	
WITCASGL 12.0	Cleanup Levels for individual hazardous substances	
MTCATPH 12.0	The Excel Workbook Version 12.0 for calculating Method B or C TPH	
WITCATFIT 12.0	Cleanup Levels	
NAPL	Nonaqueous Phase Liquid	
NBs	Natural background soil concentration	
ng/kg	nanograms per kilogram for soil media sample (same as part per trillion: ppt)	
NWTPH-Dx	Northwest total petroleum hydrocarbons – diesel range organics	
NWTPH-Gx	Northwest total petroleum hydrocarbons – gasoline range organics	
ORNL	Oak Ridge National Laboratory	
ppb	Parts per billion	
ppm	Parts per million	
PQL	Practical Quantitation Limit	
R	Ideal gas constant	
RAIS	Risk Assessment Information System	
RfD	Reference dose	
risk	Cancer or carcinogenic risk	
S	Aqueous solubility	
SGL	Single chemical	
SVOC	Semivolatile organic compound	
Т	Temperature	
TEF	Toxicity equivalent factor	
TEQ	Total toxic equivalent	

Acronym or abbreviation	Definition
TEQ	Total Toxicity Equivalence
TPH	Total Petroleum Hydrocarbon
VAF	Vapor Attenuation Factor
VBA	Visual Basic Applications
VISL	EPA's Vapor Intrusion Screening Level
VPH	Volatile petroleum hydrocarbon
WAC	Washington Administrative Code
Workbook	MTCATPH Excel-based workbook tool, Version 12.0.

Chapter 1. Introduction

The Model Toxics Control Act (MTCA) Cleanup Regulation, <u>Chapter 173-340 WAC</u>xi, sets forth the requirements and procedures for establishing cleanup levels that are protective of human health and the environment. The purpose of this User's Guide is to introduce the user to the features of the MTCATPH Version 12.0 Excel-based Workbooks for calculating Soil and Groundwater Cleanup Levels for Total Petroleum Hydrocarbon (TPH) mixtures. This guide is arranged as a set of tutorials that allow the user to learn the basics of the Workbook in a "hands-on" environment.

1.1 Overview of the MTCATPH Workbook Version 12.0

The MTCATPH Workbook Version 12.0 (also referred to as the Workbook in this document) is a tool that may be used to calculate Method B and/or Method C cleanup levels for petroleum mixtures in soil and groundwater based on protection of human health and the environment.

The MTCA regulation provides for the establishment of both standard and modified Methods B and C cleanup levels.

- Under standard Methods B and C, cleanup levels are calculated using standard
 equations and default assumptions provided in the regulation. Except for petroleum
 mixtures, cleanup levels calculated for hazardous substances under standard Methods B
 and C are published in the Washington State Department of Ecology's (Ecology) <u>Cleanup</u>
 <u>Levels and Risk Calculations</u>xii (CLARC) database.
- Under modified Methods B and C, specified default assumptions may be adjusted based on site-specific or chemical-specific data. The MTCA regulation (see <u>WAC 173-340-708</u>^{xiii} (10)) specifically describes which parameters may be adjusted and how they may be adjusted.

Note: The MTCATPH Workbook uses the standard equations and default assumptions and does not allow the user to calculate modified Methods B or C cleanup levels for petroleum mixtures. For calculating modified Methods B or C cleanup levels for individual chemicals, please see Ecology's Workbook for Calculating Cleanup Levels for Individual Hazardous Substances (MTCASGL 12.0 Excel Workbook) and the associated *User's Guide for MTCASGL Workbook Version 12.0*ⁱ, Ecology Publication 25-09-201.

For the calculation of **soil cleanup levels**, the MTCATPH Workbook provides tools for evaluating the direct contact pathway and the leaching pathway (protection of groundwater).

For the evaluation of the **direct contact pathway**, the Workbook uses the equations provided in <u>WAC 173-340-740</u>^{xiv} and <u>WAC 173-340-745</u>^{xv}. The Workbook allows the user to evaluate concurrent exposure due to ingestion and dermal contact with petroleum contaminated soil.

For the evaluation of the **leaching pathway**, the Workbook uses the 3- and 4-phase equilibrium partitioning models described in the regulation (see <u>WAC 173-340-747</u>^{xvi}) to calculate a soil cleanup level that will not cause an exceedance of the groundwater cleanup level established under <u>WAC 173-340-720</u>^{xvii}. That is, this is a soil cleanup level that is protective of groundwater beneficial uses (e.g., potable water ingestion) at the site.

For the calculation of **groundwater cleanup levels**, the Workbook provides tools for calculating only Method B potable groundwater cleanup levels, as defined in the regulation (see WAC 173-340-720).

When establishing cleanup levels for hazardous substances at a site, the site manager often asks **two types of questions**.

- Is the measured (or current) concentration at the site protective?
- If not, what is the protective concentration (i.e., cleanup level)?

The Workbook allows the user to answer both questions as discussed in Chapters 3 and 4.

This User's Guide describes the capabilities and limitations of the MTCATPH Workbook, provides step-by-step instructions for downloading and using the Workbook, and documents the methods used by Ecology to develop concentrations that meet the acceptable noncancer hazard and cancer risk (risk) levels required by the MTCA Cleanup Regulation. Noncancer hazard and risk levels are described in <u>WAC 173-340-705</u> viii (Method B) and <u>WAC 173-340-705</u> (Method C).

1.2 Getting started

1.2.1 File download

The MTCATPH 12.0 calculations are performed in a single Excel workbook, the "Workbook", which can be downloaded from Ecology's Online tools for cleaning up sites web page. Unlike the prior MTCATPH Workbook (ver. 11.1), this version (12.0) does not include a pop-up dialogue "Navigator" or other pop-up windows as the primary means for navigation but opens as a normal Excel workbook with visible worksheet tabs. After downloading the Excel file, open the workbook and make that the **Solver Add-in** is installed, and **Macros** is enabled (see below).

Install the Solver Add-in function using the steps below.

- 1. In Excel, go to File > Options.
- 2. Click Add-ins, and then in the Manage box, select Excel Add-ins, and then click Go.
- 3. In the Add-ins available box, select the Solver Add-in check box, and then click OK.
- 4. After you load the Solver Add-in, the **Solver** command is available in the **Analyze** group on the **Data** tab.

Enable Macros using the steps below.

- 1. In Excel, go to File > Options.
- 2. Click **Trust Center**, and then click **Trust Center Settings**.
- 3. In the Trust Center, click Macro Settings.
- 4. Under Macro Settings, click **Enable VBA macros**.

1.2.2 Navigating and using the workbook

Workbook features and organization are as follows:

The Workbook consists of 14 individual worksheets that include:

- Supporting information including instructions and navigation
- Data entry worksheets for soil and groundwater
- Soil calculation and cleanup level summary worksheets
- Groundwater calculation worksheets

The worksheets have been color coded as described below.

- **Green tabs**: Supporting worksheets including updates, instructions, navigation, and the chemical database.
- **Orange tabs**: Worksheets for soil data entry, Method B soil direct contact calculations, soil leaching calculations, and a soil cleanup level summary worksheet.
- Red tabs: Worksheets for Method C soil direct contact calculations.

 Blue tabs: Worksheets for groundwater data entry and Method B potable groundwater calculations.

Prior to getting started, it's recommended to closely review the green tabs labelled "Instructions" and "Navigation". Information in these worksheets provide the user with step-by-step instructions for navigating and using the workbook.

The Workbook includes a "Navigation" worksheet (green tab) that allows the user to easily navigate between worksheets using color coded buttons as shown in **Figure 1-1** below. The buttons have a hyperlink that will take the user to the designated worksheet. Alternatively, users can simply scroll to and click on individual worksheet tabs for navigation.

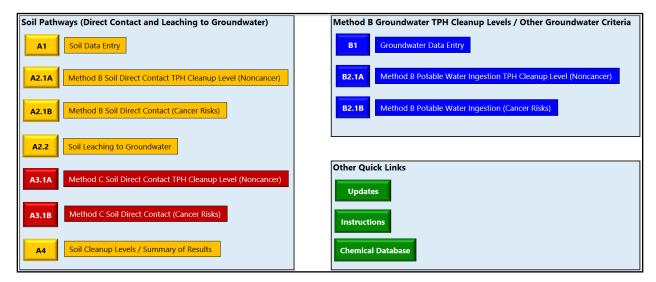


Figure 1-1: Overview of the MTCATPH Navigation Buttons

The "Navigation" worksheet provides the recommended steps for navigating the Workbook and determining soil and groundwater TPH cleanup levels. The recommended steps are also provided in the form of a flow chart in the worksheet as shown in **Figure 1-2**.

Figure 1-2: Flow Chart for Navigation and Development of TPH Cleanup Levels

Step 1: Worksheet A1 (Soil Data Entry)

- > Enter site information
- > Enter Soil TPH Data
- Enter hydrogeological data

Step 2: Worksheet B1 (GW Data Entry)

- Enter TPH Groundwater Data (if available)
 - ✓ Review worksheet B2.1A for the Method B potable water ingestion TPH cleanup level (based on a noncancer HI of 1)
- Use of Method A. The appropriate Method A TPH potable cleanup level may be used as a default when a Method B potable level has not been determined, or if it's higher than the Method B potable level***
- Determine the Target TPH GW Conc.* Enter the value and basis in Section 4 of the A1 Soil Data Entry worksheet

Note: Adjust the Target TPH GW Conc.* as appropriate to account for other pathways that may be complete (e.g., discharge to surface water)**

Step 3: Worksheets A2.1A and A3.1A (Soil Direct Contact – Noncancer)

- Review the Method B or C soil direct contact TPH cleanup levels (based on a noncancer HI of 1)
- Adjust the levels if necessary**

Step 4: Review Cancer Risks

Worksheets A2.1B and A3.1B

(Soil Direct Contact - Cancer)

- Review the Method B or C soil direct contact cancer-based risk results. Check for chemicals that contribute to unacceptable risk
- Adjust the levels if necessary**

Worksheet B2.1B

(Potable Water Ingestion - Cancer)

- Review the Method B potable groundwater cancer-based risk results. Check for chemicals that contribute to unacceptable risk
- Adjust the levels if necessary**

Step 5: Worksheet A2.2 (Soil Leaching)

- Don't evaluate soil leaching if an Empirical Demonstration is made (see 173-340-747(3)(f)). Check to meet requirements for Residual Saturation (see WAC 340-747(10)
- Use the "Calculate Soil Leaching Cleanup Level" blue button to derive a TPH soil cleanup level that is protective of the Target TPH Groundwater Concentration

Step 6: Worksheet A4

(Soil TPH Cleanup Level Summary)

- Review soil direct contact and soil leaching TPH protective levels
- Use of Method A. The appropriate Method A TPH soil cleanup level may be used as a default when it's higher than the Method B or C TPH cleanup level***
- *The User Defined Target TPH Groundwater Concentration is the same as the Groundwater Cleanup Level that may be applied to areas of the Site that correspond to a particular product type or if appropriate the whole site.
- **Soil and groundwater cleanup levels calculated using this workbook may need to be manually adjusted to account for considerations identified in Chapters 2.2.2 and 2.2.3 of the guidance manual. For example, adjustments may need to be made to account for HI and risk contributions from chemicals other than petroleum mixtures that co-exist at the site.
- *** Use of Method A TPH criteria is discussed in Section 2.3 of the MTCATPH Version 12.0 guidance. Final compliance for the groundwater standards should be conducted consistent with Section 10.3 of Ecology's Guidance for Remediation of Petroleum Contaminated Sites, Revised June 2016. Final compliance for the TPH remediation area in soil should be conducted consistent with Sections 10.1 and 10.2 of the guidance. Important: The NWTPH method (Gx or Dx) should be used for comparison to Method A TPH cleanup levels. This method may also be used to compare against site-specific total TPH cleanup levels calculated using EPH/VPH data.

Additional information provided in the Navigation tab includes.

• List of Abbreviations: This shows the list of abbreviations used in the Workbook.

• **Default Residual Saturation Screening Levels**: This shows the default residual saturation screening levels for different TPH mixtures as set forth in <u>WAC 173-340-900</u>^{xx}, Table 747-5. For a soil concentration to be protective of groundwater, the regulation requires that the concentration must not result in the accumulation of NAPL on or in the groundwater (see <u>WAC 173-340-747</u>^{xvi}(2)(b)). The default residual saturation screening levels may be used to determine whether the soil concentration calculated using the three- and four-phase models meets the regulatory requirement. Site-specific residual saturation screening levels may also be established (see WAC 173-340-747(10)).

1.2.3 Saving and closing the workbook

Once an analysis is complete, it is good practice to print out a copy (hard copy or pdf) of the results as a record. At this point, you may also wish to save the Workbook under a new name [File > Save As].

1.3 Prerequisites for use

To use the Workbook, the user should be familiar with the concept of TPH fractions and the analytical requirements for TPH mixtures. Special analyses are required for various types of TPH mixtures (see Table 830-1 in WAC 173-340-900) to adequately characterize TPH for evaluation using this Workbook tool. Depending on the type of TPH, analysis may also be required for specific volatile petroleum components (e.g., BTEX), fuel additives, semivolatile organic compounds (SVOCs), and other contaminants. A primer on TPH mixtures, fractions, and analytical requirements is included in Section 2.1.

Soil leaching pathway. The fundamental equations, associated parameters, physical-chemical properties of TPH fractions, and default values for calculating soil cleanup levels based on the leaching pathway (protection of groundwater) are set forth in WAC 173-340-747 and reproduced in **Appendices A and B**. An in-depth technical discussion of the model theory behind equilibrium partitioning for contaminants in soil leaching to groundwater is included in a separate article (Park & San Juan, 2000)¹ that can be downloaded from the U.S. Environmental Protection Agency (EPA) <u>CLU-IN</u> website².

¹ Park, Hun Seak and San Juan, Charles, 2000, A Method for Assessing Leaching Potential for Petroleum Hydrocarbons Release Sites: Multiphase and Multisubstance Equilibrium Partitioning, at https://clu-in.org/conf/tio/cra6/resources/PARKJUAN_3&4PhaseTheory.pdf

² Contaminated Site Clean-Up Information at https://clu-in.org/

1.4 Restrictions and caution on use of the workbook

The requirements and procedures for establishing cleanup levels that are protective of human health and the environment are specified in the MTCA Cleanup Regulation, <u>Chapter 173-340 WACxi</u>. The use of this User's Guide and the MTCATPH Workbook may not be sufficient to establish cleanup levels under the regulation. The Workbook is merely a computational tool and may not provide all the information necessary to establish cleanup levels for a site. Appropriate background, training, and experience are recommended to accurately use the Workbook. Available resources include guidance provided on our <u>CLARCxii</u> webpage and training via our MTCA 101 class³.

Restrictions and cautions related to use of the soil leaching models and calculating soil and groundwater cleanup levels are discussed below.

1.4.1 Soil leaching models

The Workbook uses the three- and four-phase equilibrium partitioning models to calculate soil cleanup levels that are protective of groundwater quality. Restrictions on use of the four-phase model for soil containing fuels that have been enhanced with alcohol are discussed in the MTCA Rule. See <u>WAC 173-340-747</u>^{xvi} (6)(b). Additional guidance on addressing fuel additives is provided in Section 7.10 of our <u>Guidance for Remediation of Petroleum Contaminated Sites</u>, Revised June 2016ⁱⁱ.

The four-phase model is intended for use primarily on fresh or weathered TPH mixtures. Use of the tool for other mixtures of organic compounds (a mixture of solvents and creosote compounds, for example) is not as well tested as for petroleum product applications and the results may not be as reliable. Such applications need to be thoroughly scrutinized (quality checked) to make sure the results are within reasonable bounds.

1.4.2 Calculating soil cleanup levels

The soil cleanup levels calculated using the orange and red tabbed soil worksheets account for the following.

• Soil concentrations based on **protection of the human direct contact pathway** (concurrent ingestion and dermal contact) under Methods B and C.

.

³ MTCA 101: Understanding and Applying Washington State's Model Toxics Control Act (hosted by the National Environmental Management Academy (NEMA) – check the training calendar for availability @ https://nemallc.com).

Soil concentrations based on protection of groundwater quality (leaching pathway).
 The user must develop a target TPH groundwater concentration based on the exposure pathway that generates the most stringent cleanup level (i.e., lowest concentration).
 Exposure pathways to consider (refer to your conceptual site model) are discussed below.

Potable groundwater

When using Method B or C to develop a soil cleanup level using TPH fractions, the target cleanup level for potable groundwater may be based on site-specific TPH fractionated groundwater data (Method B calculated level if available), or the appropriate Method A TPH potable groundwater cleanup level from WAC 173-340-900^{xx}, Table 720-1 may be used as a default. The higher of the two levels may be applied as the target TPH groundwater concentration for potable water ingestion.

Note: The User Defined Target TPH Groundwater Concentration is the same as the Groundwater Cleanup Level that may be applied to areas of the Site that correspond to a particular product type or if appropriate the whole site (see *Guidance for Remediation of Petroleum Contaminated Sites, Revised June 2016*ⁱⁱ, Section 8.9, Step 4).

- Protection of surface water Where contaminants in groundwater are likely to reach surface water, use the minimum cleanup level (i.e., lowest concentration) between human health and aquatic life pathways (described below) that are applicable to the site.
 - Human health fish consumption pathway. For surface waters that support or have the potential to support fish or shellfish, the MTCA Rule allows the use of Method A TPH groundwater cleanup levels (from WAC 173-340-900, Table 720-1) as the Method B surface water level (in lieu of using Equation 730-1 in WAC 173-340-730^{xxi}(3)(b)(iii)(C).
 - Potable surface water pathway. Use the potable groundwater ingestion level if surface water is suitable as a domestic water supply. See WAC 173-340-730 (3)(b)(iv).
 - Ecological pathway. Ecology's <u>Implementation Memo No. 23</u>ix (IM #23) contains gasoline and diesel surface water concentrations that are predicted to be protective of aquatic receptors in marine and freshwater using the NWTPH-Gx and NWTPH-Dx methods.

Nonpotable groundwater

Where groundwater is determined to be nonpotable and not likely to reach surface water, the potable groundwater ingestion level may still be used as a default (see <u>WAC 173-340-720</u>xvii(6)(b)(i)). In lieu of using levels based on conservative drinking water exposure, a site-specific risk assessment may be performed to develop levels based on all potential exposure pathways and groundwater use at the site (see WAC 173-340-720(6)(b)(ii)).

Caution: The soil cleanup levels calculated using the soil worksheets **DO NOT** account for the following:

- Concentrations established under applicable state and federal laws
- Natural background concentrations⁴
- Practical quantitation limits (PQLs)
- Concentrations based on protection of air quality (vapor pathway⁵)
- Concentrations based on protection of terrestrial ecological receptors
- Residual saturation limit for protection of groundwater
- Total site noncancer hazard and risk (e.g., where chemicals other than petroleum mixtures co-exist at a site, e.g., chlorinated solvents)

The soil cleanup levels calculated using the soil worksheets may need to be manually adjusted to account for these considerations (see WAC $173-340-740^{xiv}$ (5) and WAC $173-340-745^{xv}$ (6)).

1.4.3 Calculating groundwater cleanup levels

The potable groundwater cleanup levels calculated using the blue tabbed groundwater worksheets account for the following:

⁴ Natural background is generally not relevant to petroleum. Except for PAHs, which may be produced naturally during incomplete burning (e.g., forest fires), the compounds provided in the MTCATPH Workbook don't occur naturally. Ecology has not adopted a natural background level for PAHs.

⁵ To assess the vapor pathway for petroleum mixtures, see Ecology's Guidance: *Guidance for Evaluating Vapor Intrusion in Washington State: Investigation and Remedial Action* at https://apps.ecology.wa.gov/publications/SummaryPages/0909047.html

- Concentrations established under applicable state and federal laws⁶; and
- Concentrations based on protection of human health.

Caution: The potable groundwater cleanup levels calculated using the groundwater worksheets **DO NOT** account for the following:

- Natural background concentrations⁷
- PQLs
- Concentrations based on protection of air quality (vapor pathway⁸)
- Concentrations based on potential surface water impacts
- Nonaqueous phase liquid (NAPL) limitation⁹
- Total site noncancer hazard and risk (e.g., where chemicals other than petroleum mixtures exist at a site, e.g., chlorinated solvents)
- Potential concentrations of non-petroleum polar organic metabolites from weathered petroleum groundwater plumes (see Ecology's <u>Guidance for Silica Gel Cleanup in</u> <u>Washington State. November 2023. Publication No. 22-09-059</u>v)
- Biodegradation. For example, if modeling or groundwater monitoring indicates that biological degradation of residual petroleum may result in violation of the drinking water standards for other chemicals (e.g., naturally occurring metals such as arsenic, iron, and manganese). See <u>Guidance for Remediation of Petroleum Contaminated Sites,</u> <u>Revised June 2016</u>ii, Section 8.9, Step 9

The groundwater cleanup levels calculated using the groundwater worksheet may need to be manually adjusted to account for these considerations (see <u>WAC 173-340-720</u>^{xvii}(7)).

⁶ Potable groundwater cleanup levels that have been adjusted to account for levels based on applicable, relevant, and appropriate requirements (ARARs) are provided in the groundwater TPH cleanup level worksheets.

⁷ Natural background is generally not relevant to petroleum. Except for PAHs, which may be produced naturally during incomplete burning (e.g., forest fires), the compounds provided in the MTCATPH Workbook don't occur naturally. Ecology has not adopted a natural background level for PAHs.

⁸ To assess the vapor pathway for petroleum mixtures, see Ecology's Guidance: Guidance for Evaluating Vapor Intrusion in Washington State: Investigation and Remedial Action at https://apps.ecology.wa.gov/publications/SummaryPages/0909047.html

⁹ The cleanup level determined in WAC 173-340-720 shall not exceed a concentration that would result in NAPL being present in or on the groundwater. See WAC 173-340-720(7)(d).

1.5 What's new in MTCATPH Workbook Version 12.0

The most significant change between MTCATPH Workbook version 12.0 and MTCATPH version 11.1 is that version 12.0 has been updated and modernized in a new Excel based workbook tool. The MTCATPH Workbook 12.0 no longer includes a pop-up dialogue "Navigator" or other pop-up windows as the primary means for navigation but opens as a normal Excel Workbook with visible worksheet tabs. As such, version 12.0 is easier for the user to open and use (without the compatibility issues associated with Version 11.1) and will also be easier to update in the future.

Significant changes have been made to the Table in <u>Appendix B</u> of this guidance: "Properties of Chemicals commonly found at Petroleum Contaminated Sites" to incorporate updated and new scientific information. The updates reflected in Appendix B are documented in our July 2024 CLARC guidance titled: <u>Toxicity Data and Physical/Chemical Properties for Petroleum Mixtures</u>iv. Updates include changes to toxicity data and physical/chemical data used in calculating cleanup levels for petroleum mixtures. Some changes of note are provided below.

- Aliphatic (AL) >5-8 fraction: The oral toxicity surrogate for the equivalent carbon (EC)
 AL >5-8 fraction was updated from cyclohexane to cyclohexene. Cyclohexane no longer
 has an available oral reference dose (RfD), and cyclohexene, a C6 aliphatic, was
 identified by EPA in 2022 as the oral toxicity surrogate for the aliphatic low carbon
 range (i.e., AL >5-8). Cyclohexene is a constituent of gasoline and is similar structurally
 to cyclohexane. Also, these compounds have similar physical/chemical attributes.
 - **Note:** N-hexane is a C6 aliphatic and is a component of gasoline and crude oil. N-hexane's contribution to overall toxicity is separately evaluated in the Workbook using its own oral RfD. Testing for n-hexane is required when volatile petroleum hydrocarbon (VPH) analysis is performed for Method B or C (see MTCA WAC 173-340-900**, Table 830-1, Footnote 9).
- Carcinogenic polycyclic aromatic hydrocarbons (cPAHs): Toxicity data for benzo(a)pyrene (which is sometimes known as BaP) has been updated to reflect a new oral RfD and an updated oral cancer potency factor (CPF). In January 2017, EPA published several changes to the toxicity values for BaP in its Integrated Risk
 Information System xxiii (IRIS) database. EPA has also determined that BaP has a mutagenic mode of action and therefore recommends using Age-Dependent Adjustment Factors (ADAFs) to address increased childhood sensitivity (compared to adults) to its carcinogenic (cancer-causing) effects. The toxicity changes above are documented in Ecology's CLARC guidance titled Integrated Risk
 - Noncancer hazard: Although BaP has an oral RfD in EPA's IRIS, it's not included in the noncancer HI, and the TPH cleanup level calculations associated with soil direct contact, soil leaching, or ingestion of potable water pathways. BaP and associated

- cPAHs are excluded from these pathways since they are not identified as volatile organic compounds within the petroleum mixture (<u>WAC 173-340-740</u>xiv(3)(b)(iii)(B)(III)).
- Cancer risk: cPAHs are accounted for separately in the cancer risk calculations.
 Method B cancer risk calculations for BaP incorporate early-life exposure (ELE) adjustments using ADAFs. Method C cleanup equations are based on adult exposure and therefore do not incorporate ELE adjustments.
- Soil leaching: See Ecology's <u>Implementation Memorandum #10: Evaluating the Human Health Toxicity of Carcinogenic PAHs (CPAHs) using Toxicity Equivalency Factors (TEFs)</u>viii which provides guidance on evaluating the potential for cPAHs in soil to impact groundwater.
- Obuble counting: Table 8.7 in Ecology's <u>Guidance for Remediation of Petroleum Contaminated Sites, Revised June 2016</u> recommends subtracting substance concentrations from the appropriate fraction. Since individual cPAHs are excluded from the HI and soil leaching calculations, double counting is no longer an issue and the full AR EC>21-34 should be used for both soil and groundwater. That is, do not subtract out the total cPAH concentration from the AR EC>21-34 fraction.
- Inhalation toxicity criteria The previous MTCATPH version (Version 11.1) provided an option to evaluate the vapor pathway (protection of air quality) for informational purposes only. In 2022, Ecology updated our guidance for addressing vapor intrusion concerns at MTCA cleanup sites. The option to evaluate the vapor pathway has been removed from the MTCATPH 12.0 Workbook along with the inhalation toxicity criteria. To evaluate the vapor pathway for petroleum mixtures, please see our guidance titled: Guidance for Evaluating Vapor Intrusion in Washington State: Investigation and Remedial Action^{vi}.
- Criterion for the TPH soil and groundwater cleanup levels
 - Accounting for carcinogenic risk Unlike Version 11.1, the new Workbook (Version 12.0) does not include options to evaluate TPH soil and groundwater cleanup levels based on contributions from carcinogenic risk. The TPH cleanup levels calculated in the Workbook based on soil direct contact and potable water ingestion are based on a noncancer HI of 1 and are not adjusted to account for carcinogenic chemicals within the petroleum mixture. See WAC 173-340-740 xiv(3)(b)(iii)(B)(III); WAC 173-340-720 xvii(4)(b)(iii)(C).

Known or suspected carcinogenic chemicals that contribute to unacceptable risk within the petroleum mixture as calculated in the Workbook are evaluated separately and must meet compliance with soil and groundwater cleanup standards both on an individual basis (i.e., not to exceed a 1E-06 risk under Method B or 1E-05

under Method C), and when accounting for cumulative risk from multiple chemicals and pathways at the site (not to exceed a risk of 1E-05).

Calculations for the TPH cleanup level (based on the noncancer HI) and carcinogenic risk are presented on separate worksheets within the Workbook.

- O Use of Method A groundwater TPH cleanup levels When using Method B or C to develop a soil cleanup level using TPH fractions, the target cleanup level for potable groundwater may be based on site-specific TPH fractionated groundwater data (Method B calculated level if available), or the appropriate Method A TPH potable groundwater cleanup level from WAC 173-340-900**, Table 720-1 may be used as a default. The higher of the two levels may be applied as the target TPH groundwater concentration for potable water ingestion. Note: Final compliance for the groundwater standards should be conducted consistent with Section 10.3 of Ecology's *Guidance for Remediation of Petroleum Contaminated Sites, Revised June* 2016**

 2016**I Note that the NWTPH method (NWTPH-Gx or Dx) should be used for comparison to Method A TPH groundwater cleanup levels. This method may also be used to compare against site-specific total TPH cleanup levels calculated using EPH/VPH data.
- O Use of Method A soil TPH cleanup levels When using Method B or C to develop a TPH soil cleanup level using fractioned data (i.e., EPH or VPH), and the Method B or C TPH soil cleanup level for the site (or portion of the site contaminated by the same product) is less than the appropriate Method A TPH soil cleanup level from WAC 173-340-900, Table 740-1 (unrestricted land use) or Table 745-1 (industrial land use), the user may default to the appropriate Method A TPH soil value as the cleanup level. Note: Final compliance for the TPH remediation area in soil should be conducted consistent with Sections 10.1 and 10.2 of Ecology's *Guidance for Remediation of Petroleum Contaminated Sites, Revised June 2016*. It's important to keep in mind that although a soil excavation may initially be defined and driven by the TPH cleanup level, the final limits of the excavation should include compliance samples analyzed for all parameters that exceed cleanup levels for the remediation area (e.g., TPH and individual compounds like BTEX).

Important: If a Method A TPH soil cleanup level is used rather than a site-specific Method B or C TPH soil cleanup level derived using the Workbook, post-remediation soil samples should be analyzed for TPH concentrations using the NWTPH method (NWTPH-Gx or Dx). This method may also be used to compare against site-specific total TPH cleanup levels calculated using EPH/VPH data.

For Method B or C TPH soil cleanup levels derived using this Workbook, review Table 10.1 of Ecology's *Guidance for Remediation of Petroleum Contaminated Sites*,

Revised June 2016 for recommended alternatives for determining compliance with TPH concentrations.

• Soil leaching calculations – The soil leaching calculations have been simplified in Version 12.0 to include one modelling option. This modelling option is based on the site-specific composition of the petroleum mixture measured in soil, site-specific hydrogeological properties, and a user-defined target TPH groundwater concentration. Based on these inputs, the user may run the three- and four-phase equilibrium partitioning models to calculate a TPH soil cleanup level that is protective of the target TPH groundwater concentration based on the most stringent exposure pathway (refer to Section 1.4.2). The soil leaching calculations for this option are performed the same as the "Protection of Target TPH GW Co" option in the prior Workbook (Version 11.1).

Note: Use of Method 1—as described in Section 8.9 of Ecology's *Guidance for Remediation of Petroleum Contaminated Sites, Revised June 2016*ⁱⁱ - to derive a sitespecific Method B groundwater cleanup level that is protective of drinking water is no
longer an option in the soil leaching worksheet. Method 1 involves the use of EPH/VPH
soil data and the soil leaching model to calculate a predicted groundwater fractionated
composition and then a groundwater cleanup level from this fractionated composition.

Chapter 2. Overview of Equations and Parameters

The MTCATPH Workbook 12.0 (the Workbook) allows the user to use pre-established chemical and toxicity data, default exposure assumptions, and site-specific information to calculate any of the following for a **petroleum mixture**.

- Hazard and risk for the measured sample concentration: To evaluate if the measured (or current) concentration at the site is protective, the Workbook provides the tools necessary to calculate the noncancer hazard index (HI) and risk based on site-specific analytical measurements in soil or groundwater (i.e., current conditions). To calculate the HI and risk for the measured concentrations, the Workbook requires the user to enter measured soil and/or groundwater concentrations for petroleum fractions and compounds. The Workbook then automatically executes a "forward" calculation using the equations in the regulation and solving for hazard quotients (HQs) or risks. For soil measurements, the Workbook calculates the HI and risk corresponding to the direct contact pathway considering concurrent exposures via ingestion and dermal contact. For groundwater measurements, the Workbook calculates the HI and risk corresponding to the ingestion pathway (i.e., ingestion of potable water).
- Site-specific and risk-based cleanup levels for soil and groundwater: The Workbook provides the tools necessary to calculate soil cleanup levels under both Methods B and C (for soil direct contact), and groundwater cleanup levels under Method B only (for potable water ingestion). The Workbook "back-calculates" a TPH cleanup level for the petroleum mixture based on the target HI of 1. It also back-calculates a cleanup level for individual chemicals based on a noncancer HQ of 1, and an excess risk of one in a million (1 x 10⁻⁶ or 1E-06) under Method B, and one in one hundred thousand (1 x 10⁻⁵ or 1E-05) under Method C.
- The soil leaching pathway (protection of groundwater): The Workbook allows the user
 to calculate a soil TPH cleanup level that is protective of groundwater. This calculation is
 based on the site-specific composition of the petroleum mixture measured in soil, sitespecific hydrogeological properties, and a user-defined target TPH groundwater
 concentration.

Note on carcinogens: The TPH cleanup levels calculated in the Workbook for soil direct contact and potable water ingestion are based on a noncancer HI of 1 and are not adjusted to account for carcinogenic chemicals within the petroleum mixture. See <u>WAC 173-340-740</u>xivxiv (3)(b)(iii)(B)(III); <u>WAC 173-340-745</u>xv (5)(b)(iii)(B)(III); <u>WAC 173-340-745</u>xv (5)(b)(iii)(C).

Known or suspected carcinogenic chemicals that contribute to unacceptable risk within the petroleum mixture as calculated in the Workbook are evaluated separately and must meet compliance with soil and groundwater cleanup standards both on an individual basis (i.e., not to exceed a 1E-06 risk under Method B or 1E-05 under Method C), and when accounting for cumulative risk from multiple chemicals and pathways at the site (not to exceed a risk of 1E-05).

2.1 Primer on TPH fractions and analytical requirements for TPH mixtures

Unlike individual hazardous substances, petroleum hydrocarbon mixtures such as gasoline, diesel fuel, lubricating oils, etc. are comprised of thousands of chemical compounds. Typically, the concentration of these mixtures is measured as "total petroleum hydrocarbons" or "TPH" within a specific range of hydrocarbon chain lengths, such as the "gasoline range" or the "diesel range" 10. These TPH concentrations are the collective concentrations of the individual petroleum compounds within the specified range.

TPH mixtures can also contain specific chemicals of concern and, depending on the type of mixture, these specific chemicals may need to be tested to make sure a site is adequately characterized and that all cleanup requirements are considered. These include volatile compounds such as benzene, toluene, ethylbenzene, and xylenes (collectively referred to as "BTEX"), n-hexane, and naphthalene, but may also include fuel additives such as methyl tertiary-butyl ether (MTBE). Information contained in WAC 173-340-830 xxiv provides a more detailed discussion of the types of testing required for petroleum releases. Table 830-1 in WAC 173-340-900 xx is a summary of the required testing for different types of petroleum releases.

The MTCA Cleanup Regulation allows for site specific chemical characterization of released petroleum to develop a cleanup level tailored to the specific composition of petroleum present in soil or groundwater. This method, known as "TPH fractionation", measures the concentrations of twelve sub-groups or "fractions" of TPH within the released mixture and is based on work by a consortium of national experts (TPH Criteria Working Group, 1997¹¹). These fractions are defined based upon their relative average molecular "sizes", from the lighterweight (and typically more volatile and soluble) compounds to the heavier, less volatile, and soluble compounds. The measured concentrations of each of the twelve fractions are then

.

¹⁰ Fresh gasoline is generally composed of lighter carbon fractions up to Equivalent Carbon (EC) 12. Fresh diesel is generally composed of heavier fractions mostly greater than EC 12 and up to EC 34.

¹¹ TPH Criteria Working Group, 1997. Total Petroleum Hydrocarbon Criteria Working Group Series. Volume III: Selection of Representative Total Petroleum Hydrocarbon (TPH) Fractions Based on Fate and Transport Considerations, Ed.: J. B. Gustafson, J. G. Tell, and D. Orem, Amherst Scientific Publishers. **NOTE**: As of this writing, this and other volumes are available on the Internet at: https://www.aehsfoundation.org/tph-working-group-series.

assessed, together with their individual chemical and toxicological properties, to determine the appropriate TPH cleanup level. Depending on the particular TPH mixture present, certain hazardous substances (e.g., benzene, carcinogenic PAHs, or MTBE) must also be measured in addition to the individual TPH fractions.

The detailed analytical methods, including VPH (Volatile Petroleum Hydrocarbons) and EPH (Extractable Petroleum Hydrocarbons) for petroleum hydrocarbons, are described in a separate Ecology document (Publication No. ECY 97-602, <u>Analytical Methods for Petroleum Hydrocarbons</u>, 1997^{vii}).

2.2 Calculating soil cleanup levels

The soil worksheets (orange and red tabs) provide tools for evaluating the direct contact and leaching (protection of groundwater) pathways.

2.2.1 Direct contact pathway

For evaluation of the direct contact pathway, the worksheet uses the standard equations provided in <u>WAC 173-340-740</u>^{xiv} and <u>WAC 173-340-745</u>^{xv} and summarized below (see <u>Appendix</u> <u>C</u> and **Table 2-1** and **Table 2-2** below). For petroleum mixtures, evaluation of the direct contact pathway involves a concurrent evaluation of both soil ingestion and dermal contact.

Table 2-1: Method B Soil Equations (WAC 173-340-740)

Substance	Туре	Equation
TPH Mixture	Non-carcinogenic hazard	740-3
Individual Components	Non-carcinogenic hazard	740-4
Individual Components	Carcinogenic risk	740-5

Table 2-2: Method C Soil Equations (WAC 173-340-745)

Substance	Туре	Equation
TPH Mixture	Noncarcinogenic hazard	745-3
Individual Components	Noncarcinogenic hazard	745-4
Individual Components	Carcinogenic risk	745-5

For each of the parameters used in the equations, default assumptions (values) are set forth in the regulation to calculate **standard** Method B or C cleanup levels. Under **modified** Methods B and C, specified default assumptions may be adjusted based on site-specific or chemical-specific data. The MTCA regulation (see <u>WAC 173-340-708</u>xiii (10)) specifically describes which parameters may be adjusted and how they may be adjusted. However, irrespective of whether a parameter may be adjusted under the regulation, the worksheet uses the default value for

that parameter provided in the regulation. Also, the parameter is not listed in the worksheet and the user may not input data for that parameter.

As mentioned previously in <u>Section 1.5</u>, EPA has determined that BaP has a mutagenic mode of action and therefore recommends using ADAFs to address increased childhood sensitivity (compared to adults) to its carcinogenic (cancer-causing) effects. Method B cancer risk calculations for BaP incorporate ELE adjustments using ADAFs. Method C cleanup equations are based on adult exposure and therefore do not incorporate ELE adjustments. Equations and methods for applying ELE adjustments to determine risk and cleanup levels for BaP are provided in Ecology's CLARC guidance titled <u>Polycyclic Aromatic Hydrocarbons and Benzo[a]pyrene: Changes to MTCA default cleanup levels for 2017*xiii.</u>

Chemical-specific toxicological properties and exposure parameters used in the soil direct contact cleanup equations are documented in the green tabbed "Chemical Database" worksheet and in <u>Appendix B</u>. These properties are also documented in the July 2024 CLARC guidance titled: <u>Toxicity Data and Physical/Chemical Properties for Petroleum Mixtures</u>iv.

2.2.2 Leaching pathway

For evaluation of the leaching pathway, the worksheet uses the three and four-phase equilibrium partitioning models (depending upon NAPL formulation) described in the regulation (see <u>Appendix A</u>) to calculate a cleanup level that will not cause an exceedance of the target TPH groundwater concentration defined by the user and established per the requirements in <u>WAC 173-340-720</u>xviii (refer back to <u>Section 1.4.2</u>). For each of the soil or chemical parameters used in the equations, the user may input either the default value provided in the regulation, or a site-specific or chemical-specific value derived under the regulation.

Physical/chemical properties used in the soil leaching cleanup equations are documented in the green tabbed "Chemical Database" worksheet and in <u>Appendix B</u>. These properties are also documented in the July 2024 CLARC guidance titled: <u>Toxicity Data and Physical/Chemical</u>

Properties for Petroleum Mixturesiv.

2.2.3 Calculating groundwater cleanup levels

The groundwater worksheet (blue tab) uses the standard equations provided in the regulation (see <u>Appendix D</u> and **Table 2-3** below). For each of the exposure parameters used in the equations, default assumptions (values) are set forth in the regulation to calculate **standard** Method B cleanup levels. Under **modified** Method B, specified default assumptions may be adjusted based on site-specific or chemical-specific data. The MTCA regulation (see <u>WAC 173-340-708</u>xiii (10)) specifically describes which parameters may be adjusted and how they may be adjusted. However, irrespective of whether a parameter may be adjusted under the regulation, the worksheet **uses the default value** for that parameter provided in the regulation. Also,

exposure parameters are not listed in the worksheet and the user may not input data for these parameters.

Table 2-3: Method B Potable Groundwater Equations (WAC 173-340-720)

Substance	Туре	Equation
TPH Mixture	Noncarcinogenic hazard	720-3
Individual Components	Noncarcinogenic hazard	720-1
Individual Components	Carcinogenic risk	720-2

Groundwater potable ingestion risks and cleanup levels calculated for BaP under Method B incorporate ELE adjustments using ADAFs (see prior discussions in <u>Section 1.5</u> and <u>Section 2.2.1</u>).

Chemical-specific toxicological properties and exposure parameters used in the cleanup level equations for ingestion of potable groundwater are documented in the green tabbed "Chemical Database" worksheet and in Appendix B. These properties are also documented in the July 2024 CLARC guidance titled: Toxicity Data and Physical/Chemical Properties for Petroleum Mixtures.

Chapter 3. Calculating Soil TPH Cleanup Levels

3.1 Instructions on how to calculate the soil TPH cleanup levels

The "Instructions" worksheet (green tab) provides directions for calculating soil TPH cleanup levels. Calculations for the soil direct contact pathway are conducted automatically and do not require the selection of a button for executing the calculation.

Note: Soil leaching is the only pathway in the Workbook that requires the user to select a button to execute the calculation.

3.2 Entering data – A1_Soil Data Entry worksheet (orange tab)

The user is required to enter all necessary site-specific and analytical data before performing any data analysis for the soil pathways (i.e., direct contact and soil leaching). Note that at any time during the evaluation, the user can go back and change the data that has been entered.

3.2.1 Accessing the soil data entry worksheet

In the "Navigation" worksheet (green tab), select the A1 orange button to take you to the A1_Soil Data Entry worksheet. Alternatively, you can scroll to and click on the orange tabbed worksheet titled "A1_Soil Data Entry".

3.2.2 Input data – Part 1: Enter logistical site information

User-specified text format is entered here. As shown in **Figure 3-1**, enter descriptive text for the identification of a particular site (or a sample or a project) such as date, site name, sample name, and additional information (in the "REMARK" text box) if necessary. The MTCATPH Workbook does not require the user to enter information for any of these entries, as they are solely there for the benefit of the user. The site information entered in the A1_Soil Data Entry worksheet (shown in **Figure 3-1** below) is automatically carried forward to the other soil related worksheets (orange and red tabs).

Figure 3-1: Enter Site Information - Soil Sample

1. Enter Site Information		
Date:	04/15/06	
Site Name:	ABC Site	
Sample Name:	SB-1	

3.2.3 Input data – Part 2: Enter measured soil concentrations

The second part of the worksheet (illustrated in **Figure 3-2**) requires the user to input analytical data (soil concentrations: dry basis mg/kg) in the non-shaded (white) cells for the chemicals of concern and petroleum EC groups appropriate for the type of TPH mixture being evaluated.

Figure 3-2: Entering Soil Concentration Measured

		Composition
Chemical or Petroleum	Measured Soil Conc	Ratio
Fraction	mg/kg	%
AL_EC >5-6	35	4.1%
AL_EC >6-8	20	2.4%
AL_EC >8-10	40	4.7%
AL_EC >10-12	57	6.7%
AL_EC >12-16	125	14.8%
AL_EC >16-21	300	35.5%
AL_EC >21-34		0.0%
AR_EC >8-10	1	0.1%
AR_EC >10-12	24	2.8%
AR_EC >12-16	55	6.5%
AR_EC >16-21	145	17.2%
AR_EC >21-34		0.0%
Benzene	0.03	0.0%
Toluene	5	0.6%
Ethylbenzene	7	0.8%
Total Xylenes	13	1.5%
Naphthalene	15	1.8%
1-Methyl Naphthalene		0.0%
2-Methyl Naphthalene		0.0%
n-Hexane		0.0%
MTBE		0.0%
Ethylene Dibromide (EDB)		0.0%
1,2 Dichloroethane (EDC)		0.0%
Benzo(a)anthracene		0.0%
Benzo(b)fluoranthene		0.0%
Benzo(k)fluoranthene	1	0.1%
Benzo(a)pyrene	0.07	0.0%
Chrysene	1	0.1%
Dibenz(a,h)anthracene	0.05	0.0%
Indeno(1,2,3-cd)pyrene	1	0.1%
	845.15	100%

Note that the right-hand "Composition Ratio" column automatically calculates the percentage of the total mixture represented by the particular fraction/compound. Be sure that the correct and consistent units are used for all chemical concentrations (milligrams/kilogram = mg/kg = ppm) and that you use the same number of significant figures as reported by the laboratory. Leave blank or enter zero (0) for substances that are not analyzed (e.g., for gasoline, you probably would not test for the cPAHs, so these entries would all be blank or "0").

For values below the method detection limit (MDL), substitute one-half the MDL. For values above the MDL but below the PQL, use the value reported (e.g., J qualified data). However, for a hazardous substance or petroleum fraction that has never been detected in any sample at a site and is not suspected of being present at the site based on site history or other knowledge, leave blank or enter "0" for that value.

Note: All analytical data entries must be numeric values. Any text entry may cause an error.

Composition overlaps: If the sample has been analyzed using both the VPH (volatile petroleum hydrocarbons) and EPH (extractable petroleum hydrocarbons) methods, some EC fractions will have results from both methods. Instructions for handling composition overlaps is provided below.

- If both methods yield detects, use the higher value.
- If one method yields a non-detect and the other a detect, use the detected value.
- If both methods yield non-detects, use the lowest reporting limit for that fraction with one exception: If both the AR >12-13 (VPH) and AR >12-16 (EPH) fractions are non-detect, use the reporting limit for the AR >12-16 fraction.

Avoid double counting: The petroleum fractions include hazardous substances that may also be individually quantified, depending upon the type of mixture(s) present at a site (see Table 830-1 in <u>WAC 173-340-900</u>xx). If you have quantified one or more individual hazardous substances that are included in one of the TPH EC fractions, you need to make sure to subtract those concentrations from the appropriate EC fraction concentrations. Otherwise, you are "double counting" that particular substance. Necessary adjustments to EC fractions to avoid double counting are provided below.

- AL >5-6 corrected total = (Reported AL >5-6) (n-hexane concentration)
- AR >8-10 corrected total = (Reported AR >8-10) (ethylbenzene + total xylenes concentration)
- AR >10-12 corrected total = (Reported AR >10-12) (naphthalene concentration)
- AR >12-16 corrected total = (Reported AR >12-16) (1-methyl + 2-methyl naphthalene concentration)
- AR >21-34 corrected total = No adjustment necessary. See discussion on "Double Counting" in Section 1.5 under the bullet for cPAHs.

3.2.4 Input data – Part 3: Enter hydrogeological characteristics of the site

The third part of the worksheet requires the user to input default or site-specific data for the hydrogeological parameters illustrated in **Figure 3-3** below. These parameters are used to calculate a soil leaching cleanup level that is protective of groundwater (i.e., soil concentration that will not cause an exceedance of the target TPH groundwater concentration).

3. Enter Site-Specific Hydrogeological Data (MTCA defaults are provided for unsaturated soil)

Total soil porosity (n):

Volumetric water content (θ_w):

Volumetric air content (θ_a):

Soil bulk density (ρ_b):

0.43

Unitless

Unitless

Unitless

Unitless (calculated) $\longrightarrow \theta_a = n - \theta_w$ kg/L

Unitless

Unitless

0.001

20

Figure 3-3: Entering Site-specific Hydrological Data

Total soil porosity (n): Enter the default value of "0.43" or a site-specific value determined under <u>WAC 173-340-747</u>^{xvi}(6)(d)(iii)(D) using site-specific measurements. Note that the sum of the volumetric water content and the volumetric air content must equal the total soil porosity. The site-specific soil porosity may be calculated using the following equation and inputs provided in **Table 3-1**:

$$n = 1 - \frac{\rho_b}{\rho_s}$$

Table 3-1: Porosity Calculation

Fraction Organic Carbon (f_{oc}): Dilution Factor (DF):

Parameter	Definition	Default Value	Units
n	Total soil porosity	Calculated	unitless
$ ho_b^{}$	Dry soil bulk density	1.5 ¹²	kg/L
$ ho_{s}$	Soil particle specific gravity	2.65 ¹³	kg/L

Volumetric water content (θ_w **)**: For unsaturated soil conditions, enter the default value of "0.30" or enter a site-specific value derived under WAC 173-340-747(5)(d) using site-specific measurements. For saturated soil conditions, the value for θ_w is unknown and must be solved

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¹² Use the default value of 1.5 kg/L or use a site-specific value derived under WAC 173-340-747(5)(c)

¹³ Use the default value of 2.65 kg/L or use a site-specific value derived under WAC 173-340-747(6)(d)(iii)(D). A site-specific value may be derived by measuring the soil particle specific gravity using ASTM Method D854-00.

for (Excel uses Solver), and the user should leave it as 0.3 as indicated in Equation 747-6 in $\underline{\text{WAC}}$ $\underline{173-340-747}^{\text{xvi}}$ (6). This results in an initial starting point of 0.13 for the volumetric air content in the soil leaching calculation.

Volumetric air content (θ_a): The value for volumetric air content CANNOT be entered. The Workbook automatically calculates a value based on the values entered for total soil porosity (n) and volumetric water content (θ_w) using the following equation:

$$\theta_a = n - \theta_w$$

As an example, if the default values for total soil porosity (n = 0.43) and volumetric water content (θ_w = 0.3) are entered, then the "default" volumetric air content is 0.13.

Dry soil bulk density (ρ_b): Enter the default value of "1.5" or enter a site-specific value derived under WAC 173-340-747(5)(c) using site-specific measurements.

Fraction soil organic carbon (f_{oc}): The fraction of soil organic carbon is the total mass of organic carbon divided by a unit mass of soil (mass of carbon/mass of soil). Enter the default value of "0.001" or enter a site-specific value derived under WAC 173-340-747(5)(b)(i). The Workbook calculates a value for K_d^{14} using the f_{oc} value entered here and the K_{oc}^{15} value in the database using MTCA Equation 747-2: $K_d = K_{oc} \times f_{oc}$.

Soil samples that are analyzed for f_{oc} must be collected outside the area of contamination and below the root zone. The results are usually reported as percent organic carbon. The reported value can be converted to a fraction by dividing by 100.

Dilution factor (*DF***)**: Enter the applicable default value ("20" for unsaturated zone soil and "1" for saturated zone soil) or enter a site-specific value derived under WAC 173-340-747(5)(f) using site-specific estimates of infiltration and groundwater flow rate.

3.2.5 Input data – Part 4: Enter target TPH groundwater concentration

As described in <u>Section 1.4.2</u>, to evaluate the soil leaching pathway, the user must enter a target TPH groundwater concentration based on the exposure pathway that generates the most stringent cleanup level (i.e., lowest concentration). The target TPH groundwater concentration entered here is automatically carried forward to the soil leaching calculations in worksheet A2.2 Soil Leaching to Groundwater (orange tab). The user should select the basis for

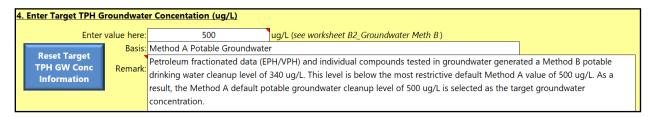
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¹⁴ K_d = Distribution coefficient (L/kg). L/kg = liters per kilogram.

¹⁵ K_{oc} = Soil organic carbon-water partitioning coefficient (L/kg).

this value from the drop-down menu provided. There is also room to add a remark to clarify the basis for the selected target TPH groundwater concentration. In the example shown in **Figure 3-4**, the Method A default potable groundwater cleanup level of $500 \,\mu\text{g/L}$ is selected as the target TPH groundwater concentration. Notes in the "Remark" section explain the rationale for selecting the default Method A potable groundwater level as the target TPH groundwater concentration. See prior <u>Section 1.4.2</u> for guidance in identifying the target TPH groundwater concentration based on potable drinking water.

Figure 3-4: Entering Target TPH Groundwater Concentration



THIS COMPLETES DATA ENTRY FOR THE SOIL WORKSHEET. SAVE YOUR WORK BEFORE CONTINUING. You should save the file under a new file name that pertains to the particular site and sample.

3.3 Soil cleanup level calculations

The soil worksheets in the MTCATPH 12.0 Workbook provide a means for evaluating the results based on the entered soil data. The following discussion on evaluating the results is **organized by worksheet**. As described previously, the Workbook allows the user to examine **two situations**.

- First, the Workbook provides the tools necessary to calculate the noncancer hazard and risk from direct contact with soil for the measured sample concentration (i.e., current conditions).
- **Second**, the Workbook provides the tools necessary to calculate soil cleanup levels based on direct contact exposure under Methods B and C. The Workbook "back-calculates" a cleanup level based on the noncancer hazard and target risk levels set forth in the regulation.

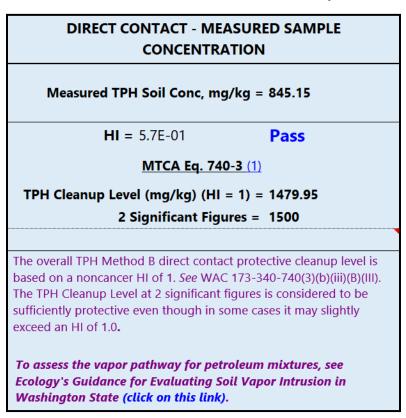
3.3.1 Worksheet A2.1A – Evaluation of the direct contact pathway (noncancer effects) under Method B (unrestricted land use)

Worksheet A2.1A presents the Method B direct contact noncancer hazard calculations and the TPH cleanup level based on an HI of 1 for the TPH mixture.

To access the worksheet: In the "Navigation" worksheet (green tab), select the A2.1A orange button to take you to the A2.1A Method B Soil Direct Contact TPH Cleanup Level worksheet. Alternatively, you can scroll to and click on the orange tabbed worksheet titled "A2.1A Soil B TPH CUL".

Direct contact noncancer hazard calculations: Results for the measured sample concentration (based on the soil data entered in Worksheet A1 Soil Data Entry) are automatically calculated as shown in two places in the worksheet (both shaded in light blue). First, a summary box (shown in **Figure 3-5**) is in the upper right-hand portion of the worksheet.

Figure 3-5: HI for Measured Concentration and TPH Cleanup Level - Method B Soil



This box provides the total concentration (mg/kg) of all the TPH fractions and compounds entered by the user (845.15 mg/kg in this example), the corresponding HI (0.57), a Pass or Fail note, the TPH cleanup level based on an HI of 1 (1,500 mg/kg), and notes for interpreting the results. In this particular example, the measured sample concentration received a "Pass" since the HI does not exceed the allowable level (i.e., HI of 1) established for Method B under WAC 173-340-705xviii(4).

Second, the four columns located to the right of the column containing measured soil concentrations (under heading: "Measured Sample Concentration"; see **Figure 3-6**¹⁶) provide the detail necessary to determine which fractions and chemicals are contributing to the HI. The sum of the individual HQs (i.e., the HI) is shown at the bottom of the column. Noncancer exceedances are noted for individual fractions and single hazardous substances that exceed an HQ of 1, and if the HI exceeds 1. Also provided are direct contact (via concurrent ingestion and dermal contact) cleanup levels based on an HQ of 1 for individual compounds detected in the soil sample.

Figure 3-6: Noncancer Hazard Details (Measured Concentration) - Method B Soil

		Measured Sa	mple Conce	ntration	
		Nor	cancer Hazard	s	
Chemical of Concern or EC group	Measured Soil Conc @dry basis	Noncancer HQ MTCA Eq. 740-4 (1)	Percent Contribution to the Total HI	Noncancer Exceedances	Noncancer-based Concentration @ HQ 1
	mg/kg	unitless	percent	(2)	mg/kg
Petroleum EC Fraction					
AL_EC >5-6	35	9.47E-02	16.6%		
AL_EC >6-8	20	5.41E-02	9.5%		
AL_EC >8-10	40	5.41E-02	9.5%		
AL_EC >10-12	57	7.71E-02	13.5%		
AL_EC >12-16	125	1.69E-01	29.6%		
AL_EC >16-21	300	1.35E-03	0.2%		
AL_EC >21-34	0				
AR_EC >8-10	1	1.35E-04	0.0%		
AR_EC >10-12	24	1.62E-02	2.8%		
AR_EC >12-16	55	1.98E-03	0.3%		
AR_EC >16-21	145	8.70E-02	15.2%		
AR_EC >21-34	0				
Benzene	0.03	9.39E-05	0.0%		320
Toluene	5	8.33E-04	0.1%		6,000
Ethylbenzene	7	9.38E-04	0.2%		7,500
Total Xylenes	13	8.71E-04	0.2%		15,000
Naphthalene	15	1.24E-02	2.2%		1,200
Sum	845.15	5.71E-01	100%	HI ≤ 1	

-

¹⁶ For illustration purposes, the list of individual fractions and chemicals shown in Figure 3-6 focuses on those that contribute to the noncancer HI.

3.3.2 Worksheet A2.1B – Evaluation of the direct contact pathway (carcinogenic risk) under Method B (unrestricted land use)

Worksheet A2.1B presents the Method B direct contact cancer risk calculations for individual hazardous substances within the TPH mixture. Note that known or suspected carcinogenic chemicals that contribute to unacceptable risk within the TPH mixture are evaluated separately and must meet compliance with soil cleanup standards both on an individual basis (i.e., not to exceed a 1E-06 risk under Method B), and when accounting for cumulative risk from multiple chemicals and pathways at the site (not to exceed a risk of 1E-05). MTCA WAC 173-340-740^{xiv} Equation 740-5 is used to evaluate cancer risk for carcinogens within the petroleum mixture.

To access the worksheet: In the "Navigation" worksheet (green tab), select the A2.1B orange button to take you to the A2.1B Method B Soil Direct Contact Cancer Risk worksheet. Alternatively, you can scroll to and click on the orange tabbed worksheet titled "A2.1B_Soil B Cancer Risk".

Direct contact risk calculations: Results for the measured sample concentration (based on the soil data entered in Worksheet A1_Soil Data Entry) are automatically calculated as shown in two places in the worksheet (both shaded in light blue). First, a summary box (shown in **Figure 3-7**) is in the upper right-hand portion of the worksheet.

CANCER RISK - MEASURED SAMPLE CONCENTRATION

Measured TPH Soil Conc, mg/kg = 845.15

Cancer Risk = 2.0E-06

Exceeds Target Risk

Note for Carcinogens: Known or suspected carcinogenic chemicals that contribute to unacceptable risk within the petroleum mixture as calculated herein are evaluated separately and must meet compliance with soil cleanup standards both on an individual basis (i.e., not to exceed a 1E-06 risk under Method B), and when accounting for cumulative risk from multiple chemicals and pathways at the site (not to exceed a risk of 1E-05). MTCA Equation 740-5 is used to evaluate cancer risk for carcinogens within the petroleum mixture.

Figure 3-7: Cancer Risk (Measured Concentration) - Method B Soil

This box provides the total concentration (mg/kg) of all the TPH fractions and compounds entered by the user (845.15 mg/kg in this example), the corresponding total cancer risk (2E-06), a cancer risk exceedance note, and notes for interpreting the results. In this particular example, cPAHs generated a cancer risk of 2E-06 (see **Figure 3-8** below), which exceeds the target risk of

1E-06 established for individual hazardous substances under Method B (see <u>WAC 173-340-705</u>xviii(2) and discussion below).

Second, the four columns located to the right of the column containing measured soil concentrations (under heading: "Measured Sample Concentration"; see **Figure 3-8**¹⁷) provide the detail necessary to determine which fractions and chemicals are contributing to the risk. The sum of the individual risks (cumulative risk) is shown at the bottom of the column. Cancer exceedances are noted for individual hazardous substances that exceed a risk of 1E-06, and if the cumulative risk exceeds 1E-05. As shown in **Figure 3-8**, the cPAH concentration in soil (i.e., the total toxic equivalent concentration or TEQ¹⁸) generated a risk of 2E-06 which exceeds the MTCA Method B individual risk threshold of 1E-06. The TPH cleanup level is not adjusted because of this, but this calculation does indicate that the cPAH TEQ concentration in the sample exceeds the cPAH TEQ cleanup level. No adjustments to the cleanup levels are needed to account for multiple carcinogens since the cumulative risk is less than 1E-05. The worksheet shows that the Method B cleanup level for comparison against the cPAH TEQ concentration is 0.14 mg/kg (based on the toxicity of benzo(a)pyrene at a 1E-06 risk).

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¹⁷ For illustration purposes, only the results for chemicals that generated a cancer risk are shown on Figure 3-8. cPAHs accounted for almost 100 percent of the risk in this example.

¹⁸ The cPAH TEQ concentration shown in Figure 2-10 was derived using the toxicity equivalent factor (TEF) approach outlined in Ecology's *Implementation Memorandum No. 10* at https://apps.ecology.wa.gov/publications/SummaryPages/1509049.html

Figure 3-8: Cancer Risk Details (Measured Concentration) - Method B Soil

	Me	asured Sa	mple Con	centration	1	
		Cancer Risk				
Chemical of Concern or EC group	Measured Soil Conc @dry basis	Cancer Risk MTCA Eq. 740-5 (1)	Percent Contribution to the Total Cancer Risk	Cancer Risk Exceedances	Cancer-based Concentration @ 1E-06 Risk	
	mg/kg	unitless	percent	(2)	mg/kg	
Benzene	0.03	1.7E-09	0.1%		18	
Benzo(a)anthracene	0					
Benzo(b)fluoranthene	0					
Benzo(k)fluoranthene	1					
Benzo(a)pyrene	0.07				0.14	
Chrysene	1					
Dibenz(a,h)anthracene	0.05					
Indeno(1,2,3-cd)pyrene	1					
cPAH TEQ (using TEFs) (3), (4)	0.285	2.0E-06	99.9%	> 1E-06		
Sum	845.15	2.0E-06	100%	≤ 1E-05		

3.3.3 Worksheets A3.1A and 3.1B – Evaluation of the direct contact pathway under Method C (industrial land use)

Worksheets A3.1A and A3.1B present the Method C soil direct contact noncancer and cancer risk calculations, respectively, for individual fractions (noncancer hazard only) and individual hazardous substances within the TPH mixture.

To access the worksheets: In the "Navigation" worksheet (green tab), select the A3.1A red button (for noncancer hazards) or the A3.1B red button (for cancer risk) to see the Method C soil direct contact results. Alternatively, you can scroll to and click on the red tabbed worksheets titled "A3.1A_Soil C_TPH_CUL" or "A3.1B_Soil C_Cancer Risk".

The worksheets for evaluating the direct contact pathway under Method C (industrial land use) all have the same features as described in <u>Section 3.3.1</u> and <u>Section 3.3.2</u> above for the unrestricted land use scenario. Under Method C, cleanup levels are calculated the same as under Method B, except that cleanup levels based on human exposure are calculated using a less stringent target cancer risk for individual hazardous substances (1E-05) and less stringent default exposure assumptions based on adult exposure (see Appendix C).

3.3.4 Worksheet A2.2 – Evaluation of the soil leaching to groundwater pathway

Worksheet A2.2 presents soil leaching calculations for deriving a soil cleanup level that is protective of the target TPH groundwater concentration identified by the user. The target TPH groundwater concentration is inputted into Section 4 of the A1_Soil Data Entry worksheet (see prior Section 1.4.2 and Section 3.2.5).

Note: See discussion on Residual Saturation at the end of this section.

To access the worksheet: In the "Navigation" worksheet (green tab), select the A2.2 orange button to take you to the A2.2 Soil Leaching to Groundwater worksheet. Alternatively, you can scroll to and click on the orange tabbed worksheet titled "A2.2 Soil Leach".

Soil leaching calculations: Worksheet A2.2 allows the user to run the soil leaching partitioning model based on the measured sample concentration entered in Worksheet A1 (Soil Data Entry). The site-specific hydrogeological properties and target TPH groundwater concentration¹⁹ used in the modelling (taken from Worksheet A1) are summarized in two separate boxes as shown in **Figure 3-9** below.

Site-Specific Hydrogeological Properties previously entered: Symbol Value Units Total soil porosity: 0.43 unitless n Volumetric water content: Qw 0.3 unitless Volumetric air content: 0.13 unitless Qa Soil bulk density measured: rb 1.5 kg/L Fraction Organic Carbon: foc 0.001 unitless Dilution Factor: DF 20 unitless **Target TPH Groundwater Concentration** Target Groundwater TPH Conc, ug/L: 500 Calculate Soil Leaching Protective Condition for the Measured Sample Concentration

Figure 3-9: Soil Leaching Model Parameters

Based on the site-specific composition of the petroleum mixture measured in soil, site-specific hydrogeological properties, and a user-defined target TPH groundwater concentration, the

¹⁹ The User Defined Target TPH Groundwater Concentration is the same as the Groundwater Cleanup Level that may be applied to areas of the Site that correspond to a particular product type or if appropriate the whole site (see *Guidance for Remediation of Petroleum Contaminated Sites, Revised June 2016*, Section 8.9, Step 4) at https://apps.ecology.wa.gov/publications/SummaryPages/1009057.html.

user may calculate the soil leaching cleanup level by clicking on the "Calculate Soil Leaching Cleanup Level" blue button in the middle of the worksheet (see **Figure 3-10**).

Calculate a Soil Concentration that is
Protective of the Target TPH Groundwater
Concentration

Calculate Soil Leaching to the Target TPH Groundwater Concentration

Click button below to run Soil Leaching calculations;

Note: a target TPH Groundwater Conc must be entered in Worksheet A1_Soil Data Entry to run the soil leaching calculation.

Calculate Soil Leaching Cleanup Level

Figure 3-10: Running the Soil Leaching Model

If the message provided in **Figure 3-11** below appears while running the soil leaching model, click "Continue" to complete the calculation.

Figure 3-11: Soil Leaching Model Maximum Iteration Limit Message



Note: cPAHs are not included in the soil leaching calculations to predict a total TPH concentration protective of potable groundwater. Compliance with cPAHs in soil for the protection of groundwater is determined separately using the 3-phase partitioning model (see Ecology <u>Implementation Memo No. 10 - Evaluating the Human Health Toxicity of Carcinogenic PAHs</u> (cPAHs) Using Toxicity Equivalency Factors (TEFs)^{viii} (April 20, 2015)).

Soil leaching pathway results for the petroleum fractions and individual chemicals are provided in the worksheet (from left to right) as follows (see **Figure 3-12**).

Measured soil concentration – dry weight basis (mg/kg): These concentrations correspond to the data entered in Worksheet A1. It is provided for reference and is not changed by any of the soil leaching calculations.

Soil concentration being tested (mg/kg): These are the soil leaching concentrations calculated by the partitioning equations presented in <u>Appendix A</u>. These modelled soil concentrations are predicted to be protective of the target TPH groundwater concentration.

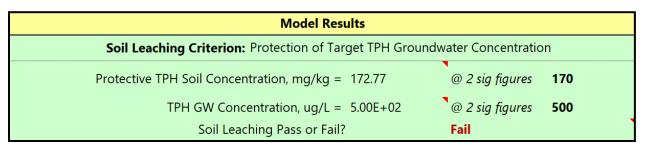
Predicted concentration at well (\mug/L): The predicted groundwater concentration based on the partitioning equations presented in <u>Appendix A</u>.

In the example calculations provided in **Figure 3-12**, based on the composition ratio of the measured soil data (total TPH concentration of 842.03 mg/kg; excludes cPAHs) and the site-specific hydrogeological parameters, the soil cleanup level predicted to be protective of a target TPH groundwater concentration of $500 \,\mu\text{g/L}$ is $172.77 \,\text{mg/kg}$ (or $170 \,\text{mg/kg}$ rounded to two significant figures). These results are also summarized in a separate box in the worksheet as illustrated in **Figure 3-13**. As shown in the example provided in **Figure 3-13**, the measured TPH concentration (excluding cPAHs) of 842.03 mg/kg "Fails" the soil leaching pathway because it exceeds the soil leaching cleanup level of 170 mg/kg determined by the model.

Figure 3-12: Soil Leaching Pathway Results

	Measured Soil Conc	Soil Leaching I	Pathway Results
Chemical of Concern or EC Group	@dry basis	Soil Conc being tested (1)	Predicted Conc @Well
	mg/kg	mg/kg	ug/L
Petroleum EC Fraction			
AL_EC >5-6	35	7.18E+00	6.38E+01
AL_EC >6-8	20	4.10E+00	8.94E+00
AL_EC >8-10	40	8.21E+00	1.49E+00
AL_EC >10-12	57	1.17E+01	1.48E-01
AL_EC >12-16	125	2.56E+01	6.01E-03
AL_EC >16-21	300	6.16E+01	1.77E-05
AL_EC >21-34	0	0.00E+00	0.00E+00
AR_EC >8-10	1	2.05E-01	3.13E+00
AR_EC >10-12	24	4.92E+00	3.60E+01
AR_EC >12-16	55	1.13E+01	2.20E+01
AR_EC >16-21	145	2.98E+01	4.79E+00
AR_EC >21-34	0	0.00E+00	0.00E+00
Benzene	0.03	6.16E-03	9.97E-01
Toluene	5	1.03E+00	1.04E+02
Ethylbenzene	7	1.44E+00	7.86E+01
Total Xylenes	13	2.67E+00	1.43E+02
Naphthalene	15	3.08E+00	3.31E+01
1-Methyl Naphthalene	0	0.00E+00	0.00E+00
2-Methyl Naphthalene	0	0.00E+00	0.00E+00
n-Hexane	0	0.00E+00	0.00E+00
MTBE	0	0.00E+00	0.00E+00
Ethylene Dibromide (EDB)	0	0.00E+00	0.00E+00
1,2 Dichloroethane (EDC)	0	0.00E+00	0.00E+00
Benzo(a)anthracene			
Benzo(b)fluoranthene			
Benzo(k)fluoranthene			
Benzo(a)pyrene		see Note (2)	
Chrysene			
Dibenz(a,h)anthracene			
Indeno(1,2,3-cd)pyrene			
Sum	842.03	1.73E+02	5.00E+02

Figure 3-13: Soil Leaching Model Results



Additional model details: A separate box (see **Figure 3-14**) located underneath the "Model Results" contains additional model simulation results for key parameters and information such as the following.

- Type of model used for computation. The spreadsheet incorporates either the three- or four-phase partitioning model. The four-phase model is applied when the presence of a NAPL phase is detected mathematically. The three-phase model solution is used where the four-phase solution is not appropriate for any given soil.
- Initial weighted average density of NAPL, kg-NAPL/L-NAPL. This is the calculated pure phase liquid density (see numerator expression in Appendix A Equation 747-8).
- Volumetric NAPL content, θ_{NAPL} (cm³-NAPL/cm³-soil). This is the estimated volume of NAPL (in cubic centimeters) per cubic centimeter of soil. The volumetric NAPL content may also be expressed as: milliliter (ml) NAPL volume/ml soil volume. This value is approximately equal to the volumetric air content if all the air space in the soil medium is filled with NAPL (i.e., 100% NAPL). For both unsaturated and saturated soil this value is unknown and must be solved for.
- NAPL saturation (%). This is the ratio of NAPL volume to total soil porosity volume. It is calculated as θ_{NAPL} /Total Soil Porosity. It's also described as the fraction of NAPL in the void space.
- 100% NAPL. TPH concentration when air space is completely filled with petroleum product.
- Mass distribution pattern @ 4-phase in soil pore system (i.e., water, air, solid, and NAPL phases). This is the predicted TPH mass distribution (expressed as a percent) in the soil pore system in all 4-phases after equilibrium partitioning.

Additional Model Details 4-Phase Model Type of model used for computation: Computation completed? Yes! Initial Weighted Average Density of NAPL, kg/L: 0.835 Volumetric NAPL Content, θ_{NAPL} (cm³-NAPL/cm³-soil): 2.7E-04 NAPL Saturation (%), θ_{NAPL} /total soil porosity (n): 0.06% 100% NAPL, mg/kg 72382.1 Mass Distribution Pattern @ 4-phase in soil pore system: Total Mass distributed in Water Phase: 1.16% in Solid: 8.69% Total Mass distributed in Air Phase: 2.75% in NAPL: 87.40%

Figure 3-14: Additional Soil Leaching Model Details

Notes on residual saturation: MTCA describes residual saturation as:

...the concentration of hazardous substances in the soil at equilibrium conditions. At concentrations above residual saturation, the NAPL will continue to migrate due to gravimetric and capillary forces and may eventually reach the groundwater, provided a sufficient volume of NAPL is released. See <u>WAC 173-340-747</u>^{xvi} (10)(b).

Soil leaching results for some petroleum compositions, especially those that include heavy fuel oils, may predict a soil-to-groundwater protective level that exceeds the theoretical maximum TPH that would be reached if all of the air space in the porous medium is filled with petroleum product. The soil concentration at this level, which is referred to as "100% NAPL", is usually well above the residual saturation level. For petroleum compositions in soil that reflect these conditions, the soil leaching result will indicate "Use Residual Saturation Conc". In this case, the user should check the regulatory requirements surrounding residual saturation as specified in WAC 173-340-747(10). MTCA Table 747-5 may be used as a default for setting residual saturation levels.

3.4 Soil cleanup level: Summary of results

Worksheet A4 (orange tab) presents a summary of the soil direct contact (Method B and C) and soil leaching results.

To access the worksheet: In the "Navigation" worksheet (green tab), select the A4 orange button to take you to the A4 Soil Cleanup Levels/Summary of Results worksheet. Alternatively, you can scroll to and click on the orange tabbed worksheet titled "A4 Soil CUL Summary".

A summary of the calculation results for the measured sample concentration (based on the soil data entered in Worksheet A1) is automatically provided in the worksheet as shown in **Figure 3-15**.

A4 Soil Cleanup Levels: Summary of Results. Refer to WAC 173-340-720, 740, 745, 747 Date: 04/15/06 Site Name: ABC Site Sample Name: SB-1 Measured Soil TPH Concentration, mg/kg: 845.15 **Summary of Calculation Results** With Measured Soil Conc. Protective TPH **Exposure Pathway** Method/Goal Conc (mg/kg) HI or Risk Pass or Fail Method B: Unrestricted Land Use TPH Soil Cleanup Level (@ HI =1) 1,500 5.7E-01 Pass Soil Direct Contact Fail Cancer Risk (1) 2.0E-06 Protection of Soil Incidental Ingestion and Dermal Contact: Method C: Industrial Land Use Human Health TPH Soil Cleanup Level (@ HI = 1) 26,000 3.2E-02 Pass 9.4E-08 Cancer Risk (1) Pass Soil Concentration Protective of Target TPH Groundwater Concentration Protective TPH Soil Concentration, mg/kg = 170 Fail Soil Leaching Protection of Groundwater Quality Target TPH Groundwater Concentration (μg/L) Method A Potable Groundwater Remark: Petroleum fractionated data (EPH/VPH) and individual compounds tested in groundwater generated a Method B potable drinking water cleanup level of 340 µg/L (see Worksheet B2.1A). This level is below the most restrictive default Method A value of 500 μg/L. As a result, the Method A default potable groundwater cleanup level of 500 μg/L is selected as the target groundwater concentration to develop a TPH concentration in soil that is protective of potable groundwater. Notes: (1) Known or suspected carcinogenic chemicals that contribute to unacceptable cancer risk within the petroleum mixture are evaluated separately and must meet compliance with soil cleanup standards both on an individual basis and and when accounting for cumulative risk from multiple chemicals and pathways at the site. See Worksheets: A2.1B and A3.1B (Soil Direct Contact); B2.1B (Potable Water Ingestion). Terrestrial Ecological Pathway: Check to determine if a simplified or site-specific Terrestrial Ecological Evaluation may be required (see WAC

Figure 3-15: Soil Cleanup Levels: Summary of Results

173-340-7490 through ~7494).

Soil leaching results: Soil leaching results are presented in the box below the soil direct contact results and include the soil leaching concentration calculated (using the soil leaching partitioning models provided in Appendix A) to be protective of the target TPH groundwater concentration (see Figure 3-9). Additional information includes a Pass or Fail note, the user defined target TPH groundwater concentration and basis, and any remarks. Information about the target TPH groundwater concentration is automatically populated in this worksheet based on the information inputted in Worksheet A1 (Soil Data Entry). In this example, based on the composition ratio of the measured soil data (TPH concentration of 845.15 mg/kg) and the site-specific hydrogeological parameters, the soil cleanup level predicted to be protective of a target TPH groundwater concentration of 500 μ g/L is 170 mg/kg. The rationale for applying the Method A TPH groundwater concentration of 500 μ g/L as the target TPH groundwater concentration is provided in the remarks. A "Fail" note is indicated because the TPH concentration in the sample exceeds the soil leaching cleanup level.

Note: Method B TPH groundwater cleanup level calculations (see <u>Chapter 4</u> below) are not summarized in Worksheet A4. The Method B TPH potable groundwater cleanup level based on a noncancer HI of 1 is identified in the worksheet if it is selected as the target TPH groundwater concentration for the soil leaching pathway. Regardless of the target TPH groundwater concentration that is selected (e.g., Method A, Method B potable, etc.), the user still needs to review the cancer-based Method B groundwater risk results for compliance with the target risk levels defined in MTCA (see Worksheet B2.1B and <u>Section 4.3.2</u> below).

Direct contact summary: The summary for soil direct contact is presented in the first box under "Exposure Pathway" and includes the following Method B and C results: the TPH cleanup level at an HI of 1, the calculated HI and cancer risk, and a Pass or Fail note. As shown in **Figure 3-15**, the measured TPH concentration of 845.15 mg/kg generates HIs of 0.57 under Method B and 0.032 under C, both of which are less than 1 and are therefore protective for noncancer effects. Calculated TPH soil cleanup levels (based on an HI of 1) are 1,500 mg/kg under Method B and 26,000 mg/kg under Method C.

Cancer risk results under Methods B and C are presented below the TPH Soil Cleanup Level and the associated noncancer results. In this example, the Method B cancer risk of 2E-06 received a "Fail" note because cPAHs generated a cancer risk of 2E-06, which exceeds the target risk of 1E-06 established for individual hazardous substances under Method B (see WAC 173-340-705 xviii (2) and Section 3.3.2). Cancer risk under Method C received a "Pass" because the cumulative risk is less than 1E-05.

Note: Known or suspected carcinogenic chemicals that contribute to unacceptable risk within the TPH mixture are evaluated separately and must meet compliance with soil cleanup standards both on an individual basis (e.g., not to exceed a 1E-06 risk under Method B), and when accounting for cumulative risk from multiple chemicals and pathways at the site (not to exceed a risk of 1E-05). MTCA Equation 740-5 in <u>WAC 173-340-740</u>^{xiv} and Equation 745-5 in <u>WAC 173-340-745</u>^{xv} are used to evaluate cancer risk for carcinogens within the petroleum mixture under Methods B and C, respectively.

Soil leaching results: Soil leaching results are presented in the box below the soil direct contact results and include the soil leaching cleanup level calculated (using the soil leaching partitioning models provided in Appendix A) to be protective of the target TPH groundwater cleanup level (see Figure 3-15). Additional information includes a Pass or Fail note, the user defined target TPH groundwater cleanup level and basis, and any remarks. Information about the target TPH groundwater cleanup level is automatically populated in this worksheet based on the information inputted in Worksheet A1 (Soil Data Entry). In this example, based on the composition ratio of the measured soil data (TPH concentration of 845.15 mg/kg) and the site-specific hydrogeological parameters, the soil cleanup level predicted to be protective of a target TPH groundwater cleanup level of 500 μ g/L is 170 mg/kg. The rationale for applying the Method A TPH groundwater concentration of 500 μ g/L as the target TPH groundwater concentration is provided in the remarks. A "Fail" note is indicated because the TPH concentration in the sample exceeds the soil leaching cleanup level.

Use of Method A soil TPH cleanup levels: When using Method B or C to develop a TPH soil cleanup level using fractioned data (i.e., EPH or VPH), and the Method B or C TPH soil cleanup level for the site (or portion of the site contaminated by the same product) is less than the appropriate Method A TPH soil cleanup level from WAC 173-340-900^{xx}, Table 740-1 (unrestricted land use) or Table 745-1 (industrial properties), the user may default to the appropriate Method A TPH soil value as the cleanup level. Note: Final compliance for the TPH remediation area in soil should be conducted consistent with Sections 10.1 and 10.2 of Ecology's *Guidance for Remediation of Petroleum Contaminated Sites, Revised June 2016*ii. It's important to keep in mind that although a soil excavation may initially be defined and driven by the TPH cleanup level, the final limits of the excavation should include compliance samples analyzed for all parameters that exceed cleanup levels for the remediation area (e.g., TPH and individual compounds like BTEX).

Important: If a Method A TPH cleanup level is used rather than a site-specific Method B or C TPH cleanup level derived using the Workbook, post-remediation soil samples should be analyzed for TPH concentrations using the NWTPH method (NWTPH-Gx or Dx). This method may also be used to compare against site-specific total TPH cleanup levels calculated using EPH/VPH data.

For Method B or C TPH cleanup levels derived using this Workbook, review Table 10.1 of Ecology's *Guidance for Remediation of Petroleum Contaminated Sites, Revised June 2016* for recommended alternatives for determining compliance with TPH concentrations.

3.4.1 Output - adjusting the results

As noted previously (see <u>Section 1.4.2</u>), the soil cleanup levels calculated using the soil worksheets **DO NOT** account for several factors. Consequently, to establish a soil cleanup level under the regulation, the cleanup level calculated using the worksheet may need to be manually adjusted to account for the following:

- Concentrations established under applicable state and federal laws (see <u>WAC 173-340-740^{xiv}(3)(b)(i)</u> or WAC 173-340-745^{xv}(5)(b)(i))
- Natural background concentrations²⁰ (see <u>WAC 173-340-700</u> xxv (6)(d))
- PQLs (see WAC 173-340-700(6)(d))
- Concentrations based on protection of air quality (vapor pathway²¹) (see WAC 173-340-740(3)(b)(iii)(C) or WAC 173-340-745(5)(b)(iii)(C))
- Concentrations based on protection of terrestrial ecological receptors (see WAC 173-340-740(3)(b)(ii) or WAC 173-340-745(5)(b)(ii))
- Residual saturation limit for protection of groundwater (see <u>WAC 173-340-747(2)(b)</u> and (10)) (see prior discussion of residual saturation provided in Section 3.3.4)
- Total site noncancer hazard and risk (see WAC 173-340-740(5)(a) or WAC 173-340-745(6)(a))

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²⁰ Natural background is generally not relevant to petroleum. Except for PAHs, which may be produced naturally during incomplete burning (e.g., forest fires), the compounds provided in the MTCATPH Workbook don't occur naturally. Ecology has not adopted a natural background level for PAHs.

²¹ To assess the vapor pathway for petroleum mixtures, see Ecology's: Guidance for Evaluating Vapor Intrusion in Washington State: Investigation and Remedial Action at https://apps.ecology.wa.gov/publications/SummaryPages/0909047.html

Chapter 4. Calculating Groundwater TPH Cleanup Levels

4.1 Instructions on how to calculate the groundwater TPH cleanup level

The "Instructions" worksheet (green tab) provides directions for calculating groundwater TPH cleanup levels. Calculations for the potable groundwater use pathway are conducted automatically and do not require the selection of a button for executing the calculation.

4.2 Entering data – B1 groundwater data entry worksheet (blue tab)

The user is required to enter all necessary analytical data before performing any data analysis for the potable groundwater ingestion pathway. Note that at any time during the evaluation, the user can go back and change the data that has been entered.

4.2.1 Accessing the groundwater data entry worksheet

In the "Navigation" worksheet (green tab), select the B1 blue button to take you to the B1_Groundwater Data Entry worksheet. Alternatively, you can scroll to and click on the blue tabbed worksheet titled "B1_Groundwater Data Entry".

4.2.2 Input data - Part 1: Enter logistical site information

User-specified text format is entered here. As shown in **Figure 4-1**, enter descriptive text for the identification of a particular site (or a sample or a project) such as date, site name, sample name, and additional information (in the "REMARK" text box) if necessary. The Workbook does not require the user to enter information for any of these entries, as they are solely there for the benefit of the user. The site information entered in the B1_Groundwater Data Entry worksheet (shown in **Figure 4-1** below) is automatically carried forward to the other groundwater related worksheets (blue tabs).

Figure 4-1: Enter Site Information - Groundwater Sample

1. Enter Site Information				
Date:	01/10/22			
Site Name:	ABC Site			
Sample Name:	MW-1			

4.2.3 Input data – Pat 2: Enter measured groundwater concentrations

The second part of the worksheet (illustrated in **Figure 4-2**) requires the user to input analytical data (groundwater concentrations: $\mu g/L$) in the non-shaded (white) cells for the chemicals of concern and petroleum EC groups appropriate for the type of TPH mixture being evaluated.

Figure 4-2: Entering Groundwater Concentration Measured

2. Enter Groundwater Concentration Measured					
		Composition			
Chemical or Petroleum	Measured GW Conc	Ratio			
Fraction	μg/L	%			
AL_EC >5-6	F-5/-	0.0%			
AL_EC >6-8		0.0%			
AL_EC >8-10	1	0.4%			
AL_EC >10-12	1	0.4%			
AL_EC >12-16	1	0.4%			
AL_EC >16-21	1	0.4%			
AL_EC >21-34	1	0.4%			
AR_EC >8-10	1	0.4%			
AR EC >10-12	1	0.4%			
AR_EC >12-16		0.0%			
AR_EC >16-21	1	0.4%			
AR EC >21-34		0.0%			
Benzene	6	2.1%			
Toluene	23	8.1%			
Ethylbenzene	23	8.1%			
Total Xylenes	200	70.6%			
Naphthalene	5	1.8%			
1-Methyl Naphthalene	2	0.7%			
2-Methyl Naphthalene	12	4.2%			
n-Hexane	2	0.7%			
MTBE	1	0.4%			
Ethylene Dibromide (EDB)		0.0%			
1,2 Dichloroethane (EDC)		0.0%			
Benzo(a)anthracene	0.01	0.0%			
Benzo(b)fluoranthene	0.1	0.0%			
Benzo(k)fluoranthene	1	0.4%			
Benzo(a)pyrene		0.0%			
Chrysene	0.2	0.1%			
Dibenz(a,h)anthracene	0.01	0.0%			
Indeno(1,2,3-cd)pyrene	0.1	0.0%			
	283.42	100%			

Note that the right-hand "Composition Ratio" column automatically calculates the percentage of the total mixture represented by the particular fraction/compound. Be sure that the correct and consistent units are used for all chemical concentrations (micrograms/liter = μ g/L = ppb)

and that you use the same number of significant figures as reported by the laboratory. Leave blank or enter zero (0) for substances that are not analyzed (e.g., for gasoline, you probably would not test for the cPAHs, so these entries would all be blank or "0").

For values below the MDL, substitute one-half the MDL. For values above the MDL but below the PQL, use the value reported (e.g., J qualified data). However, for a hazardous substance or petroleum fraction that has never been detected in any sample at a site and is not suspected of being present at the site based on site history or other knowledge, leave blank or enter "0" for that value.

Note: All analytical data entries must be numeric values. Any text entry may cause an error.

Composition Overlaps: Refer to <u>Section 3.2.3</u> for details.

Avoid Double Counting: Refer to <u>Section 3.2.3</u> for details.

THIS COMPLETES DATA ENTRY FOR THE GROUNDWATER WORKSHEET. SAVE YOUR WORK BEFORE CONTINUING. You should save the file under a new file name that pertains to the particular site and sample.

4.3 Groundwater cleanup level calculations

The groundwater worksheets in the **MTCATPH Workbook Version 12.0** provide a means for evaluating the results based on the entered groundwater data. The following discussion on evaluating the results is **organized by worksheet**. As described previously, the Workbook allows the user to examine **two situations**.

- **First**, the Workbook provides the tools necessary to calculate the noncancer hazard and risk from potable water ingestion for the measured sample concentration (i.e., current conditions).
- **Second**, the Workbook provides the tools necessary to calculate a groundwater cleanup level based on potable water ingestion under Method B. The Workbook "back-calculates" a cleanup level based on the noncancer hazard and target risk levels set forth in the regulation.

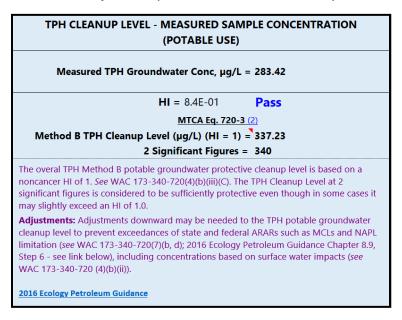
4.3.1 Worksheet B2.1A – Evaluation of the groundwater potable ingestion pathway (noncancer effects) under Method B (unrestricted land use)

Worksheet B2.1A presents the Method B potable groundwater ingestion noncancer hazard calculations and the TPH cleanup level based on an HI of 1 for the TPH mixture.

To access the worksheet: In the "Navigation" worksheet (green tab), select the B2.1A blue button to take you to the B2.1A Method B Potable Water Ingestion TPH Cleanup Level worksheet. Alternatively, you can scroll to and click on the blue tabbed worksheet titled "B2.1A GW B TPH CUL".

Potable water ingestion noncancer hazard calculations: Results for the measured sample concentration (based on the groundwater data entered in Worksheet B1_Groundwater Data Entry) are automatically calculated as shown in two places in the worksheet (both shaded in light blue). First, a summary box (see **Figure 4-3**) is located in the upper right-hand portion of the worksheet.

Figure 4-3: HI and TPH Cleanup Level (Measured Concentration) - Method B Groundwater



This box provides the total concentration (μ g/L) of all the TPH fractions and compounds entered by the user (283.42 μ g/L in this example), the corresponding HI (0.84), a "Pass" or "Fail" note, the TPH cleanup level based on an HI of 1 (340 μ g/L), and notes for interpreting the results. In this particular example, the measured sample concentration received a "Pass" since the HI does not exceed the allowable level (i.e., HI of 1) established for Method B mixtures under <u>WAC 173-340-705</u>xviii(4).

Second, the four columns located to the right of the column containing measured groundwater concentrations (under heading: "Measured Sample Concentration"; see **Figure 4-4²²**) provide the detail necessary to determine which fractions and chemicals are contributing to the HI. The sum of the individual HQs (i.e., the HI) is shown at the bottom of the column. Noncancer exceedances are noted for individual fractions and single hazardous substances that exceed an HQ of 1, and if the HI exceeds 1. Also presented are potable groundwater cleanup levels that have been adjusted to account for levels based on applicable, relevant, and appropriate requirements (ARARs; see discussion below). Exceedances of these levels are noted as ">Pot CUL" as discussed below.

Figure 4-4: Noncancer Hazard Details (Measured Concentration) - Method B Groundwater

			Measur	ed Sample Co	oncentratio	on
					Noncancer Ha	azards
Chemical of Concern or EC group	Measured GW Conc		able GW up Level (1)	Noncancer HQ MTCA Eq. 720-1 (2)	Percent Contribution to the Total HI	Noncancer Exceedances
	μg/L		μg/L	unitless	percent	(3)
Petroleum EC Fraction						
AL_EC >5-6	0					
AL_EC >6-8	0					
AL_EC >8-10	1			1.25E-02	1.5%	
AL_EC >10-12	1			1.25E-02	1.5%	
AL_EC >12-16	1			1.25E-02	1.5%	
AL_EC >16-21	1			4.17E-05	0.0%	
AL_EC >21-34	1			4.17E-05	0.0%	
AR_EC >8-10	1			1.25E-03	0.1%	
AR_EC >10-12	1			6.25E-03	0.7%	
AR_EC >12-16	0					
AR_EC >16-21	1			4.17E-03	0.5%	
AR_EC >21-34	0					
Benzene	6	5	MCL	1.88E-01	22.3%	> Pot CUL
Toluene	23	640	MCL N adj	3.59E-02	4.3%	
Ethylbenzene	23	700	MCL	2.88E-02	3.4%	
Total Xylenes	200	_	MCL N adj		14.9%	
Naphthalene	5	160	N	3.13E-02	3.7%	
1-Methyl Naphthalene	2	1.5	С	3.57E-03	0.4%	> Pot CUL
2-Methyl Naphthalene	12	32	N	3.75E-01	44.6%	
n-Hexane	2	480	N	4.17E-03	0.5%	
Sum	283.42			8.40E-01	100%	HI≤1

ARARs are considered sufficiently protective under MTCA if they are associated with less than an HQ of 1 or a risk of 1E-05. Otherwise, they must be adjusted downward so that they don't

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²² For illustration purposes, the list of individual fractions and chemicals shown in Figure 4-4 focused on those that contributed to the noncancer HI (with exception of several of the petroleum fractions).

exceed these target levels (see <u>WAC 173-340-705</u>xviii(5)). Groundwater concentrations that exceed the potable groundwater cleanup level are noted as ">Pot CUL" as shown in **Figure 4-4.** Cases where the groundwater concentration is greater than the potable groundwater cleanup level, but the HQ is less than 1, occur when the potable groundwater cleanup level is driven by the cancer endpoint or an ARAR such as a maximum contaminant level (MCL). As shown in **Figure 4-4**, although groundwater concentrations of benzene and 1-methyl naphthalene both generate HQs of less than 1, they exceed their respective potable groundwater cleanup levels. The benzene concentration exceeds its MCL (sufficiently protective at a 1E-05 risk), and 1-methyl naphthalene exceeds its groundwater cleanup level based on a risk of 1E-06 (using MTCA <u>WAC 173-340-720</u>xviii, Equation 720-2 because an MCL is not available). As such, although the TPH groundwater concentration "Passes" with an HI of less than 1, the user still needs to address potable groundwater cleanup level exceedances for benzene and 1-methylnaphthalene (see <u>Section 4.3.2</u> below).

Groundwater TPH cleanup levels protective of other criteria: The Method B groundwater calculations presented in Figure 4-3 and Figure 4-4 above apply only to potable water ingestion. As discussed previously in Section 1.4.2, the user must develop a target TPH groundwater concentration based on the exposure pathway that generates the most stringent cleanup level (i.e., lowest concentration). To assist the user in this evaluation, a separate box in the middle of Worksheet B2.1A (shaded in green) identifies options for developing groundwater TPH cleanup levels that are protective of other complete pathways at a site (e.g., protection of surface water and vapor intrusion pathways; see Figure 4-5). The most stringent TPH groundwater cleanup level is the one that is inputted in Worksheet A1 (Soil Data Entry) and used in the soil leaching calculations.

Figure 4-5: Groundwater TPH Cleanup Levels Protective of Other Criteria

Groundwater TPH Concentrations Protective of Other Criteria (μg/L)					
Surface Water - Aquatic Life					
TPH Product					
Gasoline Range Organics	1,000	1,700	Human Health		
Diesel Range Organics "Unweathered"	150	50			
Diesel Range Organics "Weathered"	3,000	2,100			

Refer to IM No. 23 for gasoline and diesel concentrations protective of surface water. (click on this link)

To assess the vapor pathway for petroleum mixtures, see Ecology's Guidance for Evaluating Soil Vapor Intrusion in Washington State (click on this link).

4.3.2 Worksheet B2.1B – Evaluation of the groundwater potable ingestion pathway (carcinogenic risk) under Method B (unrestricted land use)

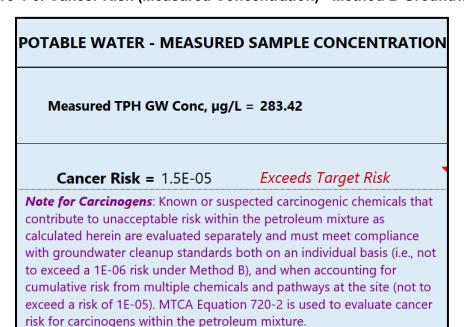
Worksheet B2.1B presents the Method B potable water ingestion cancer risk calculations for individual hazardous substances within the TPH mixture. Note that known or suspected carcinogenic chemicals that contribute to unacceptable risk within the TPH mixture are evaluated separately and must meet compliance with groundwater cleanup standards both on an individual basis (i.e., not to exceed a 1E-06 risk under Method B), and when accounting for cumulative risk from multiple chemicals and pathways at the site (not to exceed a risk of 1E-05). MTCA WAC 173-340-720^{xvii}, Equation 720-2 is used to evaluate cancer risk for carcinogens within the petroleum mixture.

To access the worksheet: In the "Navigation" worksheet (green tab), select the B2.1B blue button to take you to the B2.1B Method B Potable Water Ingestion Cancer Risk worksheet. Alternatively, you can scroll to and click on the blue tabbed worksheet titled "B2.1B_GW B Cancer Risk".

Potable water ingestion risk calculations: Results for the measured sample concentration (based on the groundwater data entered in Worksheet B1_Groundwater Data Entry) are automatically calculated as shown in two places in the worksheet (both shaded in light blue).

• **First**, a summary box (shown in **Figure 4-6**) is located in the upper right-hand portion of the worksheet.

Figure 4-6: Cancer Risk (Measured Concentration) - Method B Groundwater



This box provides the total concentration ($\mu g/L$) of all the TPH fractions and compounds entered by the user (283.42 µg/L in this example), the corresponding total cancer risk, a cancer risk exceedance note, and notes for interpreting the results. In this particular example, the cumulative risk of 1.5E-05 exceeds the target risk of 1E-05 established for multiple hazardous substances under Method B (see WAC 173-340-705 xviii (4)).

Second, the four columns located to the right of the column containing potable groundwater cleanup levels (under heading: "Measured Sample Concentration"; see Figure 4-7²³) provide the detail necessary to determine which fractions and chemicals are contributing to the risk. The sum of the individual risks (cumulative risk) is shown at the bottom of the column. Cancer exceedances are noted for individual fractions and single hazardous substances that exceed a risk of 1E-06, and if the cumulative risk exceeds 1E-05. As shown in Figure 4-7, individual risks from benzene, 1-methyl naphthalene, and cPAHs²⁴ all exceed the MTCA Method B individual risk threshold of 1E-06. These chemicals contributed over 99 percent to the cumulative risk of 1.5E-05. Also presented are potable groundwater cleanup levels that have been adjusted to account for levels based on ARARs (see discussion below), and cancer-based cleanup levels based on a 1E-06 risk.

²³ For illustration purposes, only the results for chemicals that generated a cancer risk are shown on Figure 4-7

²⁴ The cPAH TEQ concentration shown in Figure 2-24 was derived using the toxicity equivalent factor (TEF) approach outlined in Ecology's Implementation Memorandum No. 10 at https://apps.ecology.wa.gov/publications/SummaryPages/1509049.html

Figure 4-7: Cancer Risk Details (Measured Concentration) - Method B Groundwater

			Me	asured Sa	mple Conc	entration		
					Cancer Risk			
Chemical of Concern or EC group	Measured GW Conc μg/L	L	GW Cleanup evel (1) µg/L	Cancer Risk MTCA Eq. 720-2 (2) unitless	Percent Contribution to the Total Cancer Risk percent	Cancer Risk Exceedances (3)	Cancer-based Concentration @ 1E-06 Risk	
Benzene	6	5	MCL	7.5E-06	49.3%	>1E-06; >Pot CUL	0.8	
Toluene	23	640	MCL N adi					
Ethylbenzene	23	700	MCL					
Total Xylenes	200	1600	MCL N adj					
Naphthalene	5	160	N					
1-Methyl Naphthalene	2	0.86	С	2.3E-06	15.2%	>1E-06; > Pot CUL	0.9	
2-Methyl Naphthalene	12	32	N					
n-Hexane	2	480	N					
MTBE	1	24	С	4.1E-08	0.3%		24	
Ethylene Dibromide (EDB)	0	0.05	MCL					
1,2 Dichloroethane (EDC)	0	4.8	MCL C adj					
Benzo(a)anthracene	0.01							
Benzo(b)fluoranthene	0.1							
Benzo(k)fluoranthene	1							
Benzo(a)pyrene	0	0.2	MCL				0.023	
Chrysene	0.2							
Dibenz(a,h)anthracene	0.01							
Indeno(1,2,3-cd)pyrene	0.1							
cPAH TEQ (using TEFs) (5), (6)	0.124			5.4E-06	35.2%	>1E-06; see note 4		
Sum	283.42			1.53E-05	100%	> 1E-05		

ARARs are considered sufficiently protective under MTCA if they are associated with less than an HQ of 1 or a risk of 1E-05. Otherwise, they must be adjusted downward so that they don't exceed these target levels (see <u>WAC 173-340-705</u>xviii(5)). In the example shown on **Figure 4-7**, groundwater concentrations for benzene and 1-methyl naphthalene exceed their respective potable groundwater cleanup levels and are noted as ">Pot CUL".

If the potable groundwater ARAR-based cleanup levels for benzene (5 μ g/L) and cPAHs (0.2 μ g/L) and the cancer-based cleanup level for 1-methyl naphthalene (0.86 μ g/L) are input to Worksheet B1, the cumulative risk for the petroleum mixture is 1.6E-05, which exceeds the MTCA threshold of 1E-05. Therefore, although the ARAR based potable groundwater cleanup levels for benzene and cPAHs are sufficiently protective on an individual basis (i.e., less than a risk of 1E-05), further downward adjustment is needed to achieve the cumulative risk threshold of 1E-05 as required under MTCA.

Note: Only the CULs for individual carcinogenic chemicals need to be adjusted. The TPH cleanup level based on an HI of 1 does not need to be adjusted.

An example of how a downward adjustment may be made to meet the cumulative risk threshold would be to first add up the risk due to 1-methyl naphthalene at its 1E-06 cancer-

based level (0.86 μ g/L) and the risk generated by MTBE (4.1E-08). This equals a risk of 1.04E-06, which means that the combined risk from benzene and cPAHs can be set to 8.96E-06 (or 4.48E-06 for each) to achieve a cumulative risk of 1E-05.

This results in cleanup levels of 3.6 μ g/L for benzene and 0.1 μ g/L for cPAHs (rounded to 2 significant figures). Cleanup levels for benzene and cPAHs based on a risk of 4.48E-06 can be calculated using a simple proportion problem as illustrated below.

$$\text{Benzene CUL } (\frac{\mu g}{L}) = \frac{\text{Measured GW Conc} \frac{\mu g}{L} \times \text{Target Risk (i. e., 4.48E-06)}}{\text{Risk @ Measured GW Conc}}$$

Benzene CUL
$$(\frac{\mu g}{L}) = \frac{6\frac{\mu g}{L} \times 4.48\text{E}-06}{7.5\text{E}-06} = 3.58 \text{ or } 3.6 \text{ } \mu g/L$$

$$\text{cPAH CUL } (\frac{\mu g}{L}) = \frac{\text{Measured GW Conc} \left(\text{cPAH TEQ}_{25}\right) \frac{\mu g}{L} \times \text{Target Risk (i. e. , 4.48E-06)}}{\text{Risk @ Measured GW Conc}}$$

cPAH CUL (
$$\frac{\mu g}{L}$$
) = $\frac{0.124 \frac{\mu g}{L} \times 4.48 \text{E-}06}{5.4 \text{E-}06}$ = 0.103 or 0.1 $\mu g/L$

Note: The risk of 8.96E-06 does not have to be split evenly between benzene and cPAHs. Any apportionment of risk is acceptable if the cleanup level for each carcinogen does not exceed its individual starting cleanup level ("Potable GW Cleanup Level" in third column of **Figure 4-7**) and the total cancer risk summed across all carcinogens does not exceed 1E-05.

4.4 Output-adjusting the results

As noted previously (see <u>Section 1.4.3</u>), the potable groundwater cleanup levels calculated using the groundwater worksheets DO NOT account for several factors. Consequently, to establish a potable groundwater cleanup level under the regulation, the cleanup level calculated using the worksheets may need to be manually adjusted to account for the following:

²⁵ The "cPAH TEQ" concentration is derived using the toxicity equivalent factor (TEF) approach outlined in Ecology's Implementation Memorandum No. 10.

https://apps.ecology.wa.gov/publications/documents/1509049.pdf

This concentration represents the total toxic equivalent (TEQ) concentration for the cPAH mixture and is compared to the cleanup level for benzo(a)pyrene. cPAH = Carcinogenic Polycyclic Aromatic Hydrocarbons

- Natural background concentrations²⁶ (see <u>WAC 173-340-700</u>^{xxv}(6)(d))
- PQLs (see WAC 173-340-700(6)(d))
- Concentrations based on protection of air (vapor pathway²⁷) (see <u>WAC 173-340-720</u>xvii(1)(d)(iv))
- Concentrations based on potential surface water impacts (see WAC 173-340-720(4)(b)(ii) and (5)(b)(ii))
- Nonaqueous phase liquid (NAPL) limitation²⁸ (see WAC 173-340-720(7)(d))
- Total site noncancer hazard and risk (see WAC 173-340-720(7)(a))
- Potential concentrations of non-petroleum polar organic metabolites from weathered petroleum groundwater plumes (see Ecology's <u>Guidance for Silica Gel Cleanup in</u> <u>Washington State. November 2023. Publication No. 22-09-059</u>v)
- Biodegradation. For example, if modeling or groundwater monitoring indicates that biological degradation of residual petroleum may result in violation of the drinking water standards for other chemicals (e.g., naturally occurring metals such as arsenic, iron, and manganese). See <u>Guidance for Remediation of Petroleum Contaminated Sites,</u> <u>Revised June 2016</u>; Section 8.9, Step 9

²⁶ Natural background is generally not relevant to petroleum. Except for PAHs, which may be produced naturally during incomplete burning (e.g., forest fires), the compounds provided in the MTCATPH Workbook don't occur naturally. Ecology has not adopted a natural background level for PAHs.

²⁷ To assess the vapor pathway for petroleum mixtures, see Ecology's Guidance: Guidance for Evaluating Vapor Intrusion in Washington State: Investigation and Remedial Action at https://apps.ecology.wa.gov/publications/SummaryPages/0909047.html

²⁸ The cleanup level determined in WAC 173-340-720 shall not exceed a concentration that would result in NAPL being present in or on the groundwater. See WAC 173-340-720(7)(d).

Appendix A: Equations and Default Values for Calculating Soil Cleanup Levels Based on the Leaching Pathway (Protection of Groundwater)

THREE-PHASE PARTITIONING

Equation 747-1: Three-Phase Partitioning Equilibrium Equation.

$$C_s = C_w \times UCF \times DF \times \left[K_d + \frac{\theta_w + \theta_a \times H_{cc}}{\rho_b} \right]$$

Parameter	Definition	Default Value (Unsaturated Zone)	Default Value (Saturated)	Units
C_{s}	Soil concentration	(calculated)	(calculated)	mg/kg
C_w	Groundwater cleanup level established under WAC 173-340-720	Chem-specific	Chem-specific	μg/L
UCF	Unit conversion factor	1E-3	1E-3	mg/ug
DF	Dilution factor	20	1	unitless
K_d	Distribution coefficient	Chem-specific (1)	Chem-specific (1)	L/kg
θ_w	Water-filled soil porosity	0.3	0.43 (3)	unitless, ml/ml
θ_a	Air-filled soil porosity	0.13	Zero	unitless, ml/ml
H_{cc}	Henry's law constant	Chem-specific (2)	Chem-specific (2)	unitless
$ ho_b$	Dry soil bulk density	1.5	1.5	kg/L

Notes:

- (1) For K_d , the regulation specifies default values for certain chemicals. It also has procedures for establishing chemical-specific values. See WAC 173-340-747^{xvi}(4)(c).
- (2) For H_{cc} , the regulation specifies default values for certain chemicals. It also has procedures for establishing chemical-specific values. See WAC 173-340-747(4)(d).
- (3) To evaluate saturated soil conditions in the Workbook, the value for $\theta_{\it w}$ is unknown and must be solved for (Excel uses Solver), and the user should leave it as 0.3 as indicated in Equation 747-6 of WAC 173-340-747(6). This results in an initial starting point of 0.13 for the volumetric air content in the soil leaching calculation.

Equation 747-2: Derivation of a Distribution Coefficient (K_d) for Organic Hazardous Substances Based on the Soil Organic Carbon-Water Partitioning Coefficient (K_{oc})

$$K_d = K_{oc} \times f_{oc}$$

Parameter	Definition	Default Value	Units
K_d	Distribution coefficient	(Calculated or site-specific)	L/kg
Koc	Soil organic carbon-water partitioning coefficient	Chem-specific (1)	L/kg
f_{oc}	Soil fraction of organic carbon	0.001	unitless, g/g

Note:

(1) For K_{oc} , the regulation specifies default values for certain chemicals. It also has procedures for establishing chemical-specific values. See <u>WAC 173-340-747</u>^{xvi}(4)(c)(i).

Equation 747-3: Deriving a Dilution Factor from Site-Specific Estimates of Infiltration and Groundwater Flow Volume

$$DF = \frac{\left(Q_p + Q_a\right)}{Q_p} = 1 + \frac{Q_a}{Q_p}$$

Parameter	Definition	Default Value	Units
DF	Dilution factor	(calculated)	unitless
Q_p	Flowrate of water infiltrating (see Equation 747-5)	(calculated)	m³/yr
Q_a	Ground water flowrate (see Equation 747-4)	(calculated)	m³/yr

Equation 747-4: Calculating Groundwater Flowrate (Q_a)

$$Q_a = K \times A \times I$$

Parameter	Definition	Default Value	Units
Q_a	Ground water flowrate	(calculated)	m³/yr
K	Hydraulic conductivity	Site-specific measurement	m/yr
A	Cross-sectional area of aquifer mixing zone (1)	Site-specific measurement	m²
I	Hydraulic gradient	Site-specific measurement	unitless, m/m

Note:

(1) The aquifer mixing zone thickness shall not exceed 5 meters in depth and be equal to a unit width of 1 meter, unless it can be demonstrated empirically that the mixing zone thickness exceeds 5 meters.

Equation 747-5: Calculating the Flowrate of Water Infiltrating (Q_p)

$$Q_p = L \times W \times Inf$$

Parameter	Definition	Default Value	Units
Q_p	Flowrate of water infiltrating	(calculated)	m³/yr
L	Estimated length of contaminant source area parallel to groundwater flow	Site-specific measurement	m
W	Unit width of contaminant source area	1.0	m
Inf	Infiltration rate	Site-specific measurement (1)	m/yr

Note:

(1) A default value may be used for infiltration rate. For sites **west** or **east** of the Cascade Mountains, the default annual infiltration value shall be **70 percent** or **25 percent**, respectively, of the average annual precipitation amount.

FOUR-PHASE PARTITIONING

Equation 747-6: Conservation of Volume Equation.

$$n = \theta_w + \theta_a + \theta_{NAPL}$$

Parameter	Definition
n	Total soil porosity (ml total pore space/ml total soil volume). Use a default value of 0.43 ml/ml or use a value determined from site-specific measurements.
$ heta_{\!\scriptscriptstyle W}$	Volumetric water content (ml water/ml soil). For unsaturated soil use a default value of 0.3 or a value determined from site-specific measurements. For saturated soil this value is unknown and must be solved for. Volumetric water content equals the total soil porosity minus volume occupied by the NAPL.
$ heta_{a}$	Volumetric air content (ml air volume/ml total soil volume). For unsaturated soil this value is unknown and must be solved for. Volumetric air content equals the total soil porosity minus the volume occupied by the water and NAPL. For saturated soil this value is zero.
hetanapl	Volumetric NAPL content (ml NAPL volume/ml total soil volume). For both unsaturated and saturated soil this value is unknown and must be solved for.

Equation 747-7: Four-Phase Partitioning Equilibrium Equation

$$\frac{M_T^i}{m_{soil}} = \frac{x_i S_i}{\rho_b} \left[\theta_w + K_{oc}^i f_{oc} \rho_b + H_{cc}^i \theta_a + \frac{GFW_i}{S_i} \rho_{NAPL} \theta_{NAPL} \right]$$

Parameter	Definition
M_T^i	Total mass of each component in the system (mg). This value is derived from site-specific measurements.
m_{soil}	Total soil mass (kg). This value is derived from site-specific measurements.
x_i	Mole fraction (at equilibrium) of each component (dimensionless). This value is unknown and must be solved for.
S_i	Water Solubility of each component (mg/L). See <u>WAC 173-340-900</u> xx, Table 747-4 for petroleum hydrocarbons; see the scientific literature for other hazardous substances.
ρ_b	Dry soil bulk density (default is 1.5 kg/L).
$\theta_{\!\scriptscriptstyle W}$	Volumetric water content (ml water/ml soil).
K_{oc}^i	Soil organic carbon-water partitioning coefficient for each component (L/kg). See <u>Table 747-4</u> for petroleum hydrocarbons; see <u>WAC 173-340-747</u> ^{xvi} (4)(b) for other hazardous substances.
f_{oc}	Mass fraction of soil natural organic carbon (default is 0.001 g organic carbon/g soil).
H_{cc}^i	Henry's law constant for each component (dimensionless). See WAC 173-340-900, Table 747-4 for petroleum hydrocarbons; see WAC 173-340-747(4)(c) for other hazardous substances.
GFW_i	Gram formula weight, or molecular weight of each component (mg/mol). See WAC 173-340-900, Table 747-4 for petroleum hydrocarbons; see the scientific literature for other hazardous substances.
$ ho_{NAPL}$	Molar density of the mixture (mol/L). See WAC 173-340-747, Equation 747-8.
$ heta_{NAPL}$	Volumetric NAPL content (ml NAPL volume/ml total soil volume).
Component	For petroleum mixtures, this means the petroleum fractions, and organic hazardous substances with a reference dose; for other hazardous substances, this means each organic hazardous substance that is found in the NAPL.

Equation 747-8: Molar Density Equation

$$\rho_{NAPL} = \frac{\left[\frac{\sum x_i GFW_i}{\sum x_i GFW_i} / \left(\sum x_i GFW_i / \rho_i\right)\right]}{\sum x_i GFW_i}$$

$$= \frac{1}{\sum (x_i GFW_i / \rho_i)}$$

Parameter	Definition
$ ho_{NAPL}$	Molar density of the mixture (mol/L).
GFW_i	Gram formula weight, or molecular weight of each component (mg/mol). See <u>WAC 173-340-900</u> xx, Table 747-4 for petroleum hydrocarbons; see the scientific literature for other hazardous substances.
x_i	Mole fraction (at equilibrium) of each component (dimensionless) after equilibration. This value is unknown and must be solved for.
$ ho_i$	Density of each component (mg/L). See WAC 173-340-900, Table 747-4 for petroleum hydrocarbons; see the scientific literature for other hazardous substances.
Component	For petroleum mixtures, this means the petroleum fractions plus organic hazardous substances with a reference dose; for other hazardous substances, this means each organic hazardous substance that is found in the NAPL.

Appendix B: Properties of Chemicals Commonly Found at Petroleum Contaminated Sites

TPH Excel Workbook Chemical Database - Updated July 2024

				Oral Reference Dose	Dermal Reference Dose	Inhalation Correction Factor	Dermal Absorption Fraction	Gastrointestinal Absorption Conversion Factor	Oral Cancer Potency Factor	Dermal Cancer Potency Factor	Molecular Weight	Aqueous Solubility	Henry's Law Constant	Soil Organic Carbon-Water Partitioning Coef	Liquid Density
				(RfDo)	(RfDd)	(INH)	(ABS)	(GI)	(CPFo)	(CPFd)	GFW	s	H ee	K ".	ρ
CAS	Chemical or Petroleum Fraction	Toxicity Surrogate Chemical (EC Fractions); Other Notes	Equivalent Carbon Number	mg/kg-day	mg/kg-day	unitless	unitless	unitless	kg-day/mg	kg-day/mg	mg/mol	mg/L	unitless	L/kg	mg/L
	Petroleum EC Fraction			·		,			,					,	
110-83-8	AL_EC > 5-6	Cyclohexene (1)	5.5	0.005	0.004	2	0.03	0.8	NTV	NTV	8.100E+04	3.600E+01	3.300E+01	8.000E+02	6.700E+05
110-83-8	AL_EC > 6-8	Cyclohexene (1)	7	0.005	0.004	2	0.03	0.8	NTV	NTV	1.000E+05	5.400E+00	5.000E+01	3.800E+03	7.000E+05
	AL_EC >8-10	see note (2)	9	0.01	0.008	2	0.03	0.8	NTV	NTV	1.300E+05	4.300E-01	8.000E+01	3.020E+04	7.300E+05
	AL_EC > 10-12	see note (2)	11	0.01	0.008	2	0.03	0.8	NTV	NTV	1.600E+05	3.400E-02	1.200E+02	2.340E+05	7.500E+05
	AL_EC > 12-16	see note (2)	14	0.01	0.008	2	0.03	0.8	NTV	NTV	2.000E+05	7.600E-04	5.200E+02	5.370E+06	7.700E+05
	AL_EC > 16-21	White Mineral Oil	19	3	2.4	2	0.03	0.8	NTV	NTV	2.700E+05	1.300E-06	4.900E+03	9.550E+09	7.800E+05
8012-95-1	AL_EC > 21-34	White Mineral Oil	28	3	2.4	2	0.03	0.8	NTV	NTV	4.000E+05	1.500E-11	1.000E+05	1.070E+10	7.900E+05
98-82-8	AR_EC >8-10	Cumene	9	0.1	0.08	2	0.03	0.8	NTV	NTV	1.200E+05	6.500E+01	4.800E-01	1.580E+03	8.700E+05
91-20-3	AR_EC > 10-12	Naphthalene	10	0.02	0.016	2	0.03	0.8	NTV	NTV	1.300E+05	2.500E+01	1.400E-01	2.510E+03	9.000E+05
92-52-4	AR_EC > 12-16	1,1-Biphenyl	14	0.5	0.25	2	0.1	0.5	NTV	NTV	1.500E+05	5.800E+00	5.300E-02	5.010E+03	1.000E+06
	AR_EC > 16-21	Pyrene	19	0.03	0.015	2	0.1	0.5	NTV	NTV	1.900E+05	5.100E-01	1.300E-02	1.580E+04	1.160E+06
	AR_EC >21-34	Fluoranthene	28	0.04	0.02	1	0.1	0.5	NTV	NTV	2.400E+05	6.600E-03	6.700E-04	1.260E+05	1.300E+06
71-43-2	Benzene		6.5	0.004	0.00388	2	0.0005	0.97	0.055	0.056701031	7.800E+04	1.750E+03	1.339E-01	6.200E+01	8.765E+05
108-88-3	Toluene		7.6	0.08	0.08	2	0.03	1	NTV	NTV	9.200E+04	5.260E+02	1.485E-01	1.400E+02	8.669E+05
100-41-4	Ethylbenzene		8.5	0.1	0.092	2	0.03	0.92	NTV	NTV	1.060E+05	1.690E+02	1.643E-01	2.040E+02	8.670E+05
1330-20-7	Total Xylenes		8.67	0.2	0.184	2	0.03	0.92	NTV	NTV	1.060E+05	1.710E+02	1.414E-01	2.330E+02	8.752E+05
91-20-3	Naphthalene		11.69	0.02	0.0178	2	0.13	0.89	NTV	NTV	1.280E+05	3.100E+01	8.319E-03	1.191E+03	1.145E+06
90-12-0	1-Methyl Naphthalene			0.07	0.0623	2	0.13	0.89	0.051	0.057303371	1.422E+05	2.580E+01	8.162E-03	2.528E+03	1.020E+06
91-57-6	2-Methyl Naphthalene			0.004	0.00356	2	0.13	0.89	NTV	NTV	1.422E+05	2.460E+01	7.002E-03	2.478E+03	1.006E+06
110-54-3	n-Hexane		6	0.06	0.048	2	0.0005	0.8	NTV	NTV	8.600E+04	9.500E+00	4.468E+01	3.410E+03	6.594E+05
1634-04-4	MTBE			NTV	NTV	2	0.0005	0.8	0.0018	0.00225	8.800E+04	5.000E+04	1.122E-02	1.090E+01	7.440E+05
106-93-4	Ethylene Dibromide (EDB)			0.009	0.0072	2	0.03	0.8	2	2.5	1.879E+05	3.910E+03	1.411E-02	6.600E+01	2.168E+06
107-06-2	1,2 Dichloroethane (EDC)			0.006	0.0048	2	0.03	0.8	0.091	0.11375	9.896E+04	8.600E+03	2.755E-02	3.800E+01	1.245E+06
56-55-3	Benzo(a)anthracene	(3)		NTV	NTV	1	0.13	0.89	0.1	0.112359551	2.283E+05	9.400E-03	9.597E-05	3.575E+05	1.274E+06
205-99-2	Benzo(b)fluoranthene	(3)		NTV	NTV	1	0.13	0.89	0.1	0.112359551	2.523E+05	1.500E-03	6.040E-06	5.994E+05	1.300E+06
207-08-9	Benzo(k)fluoranthene	(3)		NTV	NTV	1	0.13	0.89	0.1	0.112359551	2.523E+05	8.000E-04	4.276E-06	5.874E+05	1.300E+06
50-32-8	Benzo(a)pyrene			0.0003	0.000267	1	0.13	0.89	1	1.123595506	2.523E+05	1.620E-03	3.607E-06	9.688E+05	1.351E+06
218-01-9	Chrysene	(3)		NTV	NTV	1	0.13	0.89	0.01	0.011235955	2.283E+05	2.000E-03	3.873E-05	1.805E+05	1.274E+06
53-70-3	Dibenz(a,h)anthracene	(3)		NTV	NTV	1	0.13	0.89	0.1	0.112359551	2.784E+05	2.490E-03	7.446E-07	1.789E+06	1.282E+06
193-39-5	Indeno(1,2,3-cd)pyrene	(3)		NTV	NTV	1	0.13	0.89	0.1	0.112359551	2.763E+05	1.900E-04	2.093E-06	1.951E+06	1.400E+06

Notes:

(1) Cyclohexane no longer has an available RfD, and cyclohexene, a C6 aliphatic, is applied as the toxicity surrogate for the oral RfD for the aliphatic EC 5 to EC 8 fraction. Cyclohexene was identified by EPA in 2022 as the oral toxicity surrogate for this fraction (EPA, 2022). Cyclohexene is a constituent of gasoline and is similar structurally to cyclohexane. Also, these compounds have similar physical/chemical attributes.

Note: N-hexane is a C6 aliphatic and is a component of gasoline and crude oil. N-hexane's contribution to overall toxicity is separately evaluated in the Workbook using its own oral 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).

(2) EPA's 2022 PPRTV for midrange aliphatic hydrocarbon streams (EC>8-EC16) (EPA, 2022).

(3) A toxicity equivalence factor (TEF) was applied to adjust the oral cancer potency factor based on the relative potency to benzo(a) pyrene. See Ecology Implementation Memo #10 - Evaluating the Human Health Toxicity of Carcinogenic PAHs (cPAHs) Using Toxicity Equivalency Factors (TEFs).

EPA, 2022. Provisional Peer-Reviewed Toxicity Values (PPRTV) for Complex Mixtures of Aliphatic and Aromatic Hydrocarbons (CASRN Various). EPA/690/R-22/003F. September 2022.

NTV = No Toxicity Value

Appendix C: Equations and Default Values for Calculating Soil Cleanup Levels Based on Direct Contact Pathway

Equations 740-3 and 745-3 (<u>WAC 173-340-740</u>^{xiv} and <u>WAC 173-340-745</u>^{xv}): Soil Direct Contact (Ingestion + Dermal) – Petroleum Mixtures (Noncarcinogenic Effects)

$$C_{soil} = \frac{HI \times ABW \times AT}{EF \times ED \times \left[\left(\frac{SIR \times AB1}{10^6 mg/kg} \sum_{i=1}^n \frac{F_{(i)}}{RfD_{o(i)}} \right) + \left(\frac{SA \times AF}{10^6 mg/kg} \sum_{i=1}^n \frac{F_{(i)} \times ABS_{d(i)}}{RfD_{d(i)}} \right) \right]}$$

Parameter	Definition	Default Value Method B Equation 740-3	Default Value Method C Equation 745-3	Units
C_{soil}	TPH soil cleanup level	(calculated)	(calculated)	mg/kg
HI	Hazard index	1	1	unitless
ABW	Average body weight over the exposure duration	16	70	kg
AT	Averaging time	6.0	20	years
EF	Exposure frequency	1.0	0.7	unitless
ED	Exposure duration	6.0	20	years
SIR	Soil ingestion rate	200	50	mg/day
AB1	Gastrointestinal absorption fraction	1.0	1.0	unitless
$F_{(i)}$	Fraction (by weight) of petroleum component (i)	Chemical- specific	Chemical- specific	unitless
SA	Dermal surface area	2,200	2,500	cm ²
AF	Adherence factor	0.2	0.2	mg/cm²- day
$ABS_{d(i)}$	Dermal absorption fraction for petroleum component (i).	See Note (1)	See Note (1)	unitless
$RfD_{o(i)}$	Oral reference dose for petroleum component (i)	Chemical- specific	Chemical- specific	mg/kg- day
$RfD_{d(i)}$	Dermal reference dose for petroleum component (i)	See Note (2)	See Note (2)	mg/kg- day
GI	Gastrointestinal absorption conversion factor	See Note (3)	See Note (3)	unitless

Parameter	Definition	Default Value Method B Equation 740-3	Default Value Method C Equation 745-3	Units
n	The number of petroleum components (petroleum fractions plus volatile organic compounds with an RfD_o) present in the petroleum mixture (See Table 830-1.)	Mixture-specific	Mixture-specific	unitless

Notes:

- (1) May use chemical-specific values or the following defaults: 0.0005 for volatile petroleum components with vapor pressure ≥ benzene; 0.03 for volatile petroleum components with vapor pressure < benzene; 0.1 for other petroleum components. See <u>Appendix B</u>.
- (2) Derived by $RfD_o \times GI$ (see note3)
- (3) May use chemical-specific values or the following defaults: 0.8 for volatile petroleum components; 0.5 for other petroleum components. See **Appendix B**.

Equations 740-4 and 745-4: Soil Direct Contact (Ingestion + Dermal) – Noncarcinogens

For hazardous substances that are part of a petroleum mixture, cleanup levels based on noncancer effects must be calculated using <u>WAC 173-340-740</u>^{xiv}, **Equation 740-4** under Method B, and <u>WAC 173-340-745</u>^{xv}, **Equation 745-4** under Method C. These equations differ from Equation WAC 173-340-740, **Equation 740-1** by including the dermal contact pathway. See WAC 173-340-740(3)(b)(iii)(B)(III) and 173-340-745(5)(b)(iii)(B)(III).

$$C_{soil} = \frac{HQ \times ABW \times AT}{EF \times ED \times \left[\left(\frac{1}{RfD_o} \times \frac{SIR \times AB1}{10^6 mg/kg} \right) + \left(\frac{1}{RfD_d} \times \frac{SA \times AF \times ABS_d}{10^6 mg/kg} \right) \right]}$$

Parameter	Definition	Default Value Method B Equation 740-4	Default Value Method C Equation 745-4	Units
C_{soil}	Soil cleanup level	(calculated)	(calculated)	mg/kg
HQ	Hazard quotient	1	1	unitless
ABW	Average body weight over the exposure duration	16	70	kg
AT	Averaging time	6.0	20	years
EF	Exposure frequency	1.0	0.7	unitless
ED	Exposure duration	6.0	20	years
SIR	Soil ingestion rate	200	50	mg/day
AB1	Gastrointestinal absorption fraction	1.0	1.0	unitless
SA	Dermal surface area	2,200	2,500	cm ²
AF	Adherence factor	0.2	0.2	mg/cm ² -day
ABS_d	Dermal absorption fraction	See Note (1)	See Note (1)	unitless
RfD_o	Oral reference dose	Chemical-specific	Chemical-specific	mg/kg-day
RfD_d	Dermal reference dose	See Note (2)	See Note (2)	mg/kg-day
GI	Gastrointestinal absorption conversion factor	See Note (3)	See Note (3)	unitless

Notes:

(1) May use chemical-specific values or the following defaults: 0.01 for inorganic hazardous substances; 0.0005 for volatile organic compounds with vapor pressure ≥ benzene; 0.03

for volatile organic compounds with vapor pressure < benzene; 0.1 for other hazardous substances. See <u>Appendix B</u>.

- (2) Derived by **RfDo** x **GI** (see note 3)
- (3) May use chemical-specific values or the following defaults: 0.2 for inorganic hazardous substances; 0.8 for volatile organic compounds; 0.5 for other organic hazardous substances. See **Appendix B**.

Equations 740-5 and 745-5: Soil Direct Contact (Ingestion + Dermal) – Carcinogens

For hazardous substances that are part of a petroleum mixture, cleanup levels based on cancer effects must be calculated using Equations 740-5 and 745-5. These equations differ from Equation 740-2 by including the dermal contact pathway. See <u>WAC 173-340-</u> 740^{xiv}(3)(b)(iii)(B)(III) and <u>WAC 173-340-745</u>xv(5)(b)(iii)(B)(III).

$$C_{soil} = \frac{RISK \times ABW \times AT}{EF \times ED \times \left[\left(\frac{SIR \times AB1 \times CPF_o}{10^6 mg/kg} \right) + \left(\frac{SA \times AF \times ABS_d \times CPF_d}{10^6 mg/kg} \right) \right]}$$

Parameter	Definition	Default Value Method B Equation 740-5	Default Value Method C Equation 745-5	Units
C_{soil}	Soil cleanup level	(calculated)	(calculated)	mg/kg
RISK	Acceptable cancer risk level	1.0E-6	1.0E-5	unitless
ABW	Average body weight over the exposure duration	16	70	kg
AT	Averaging time	75	75	years
EF	Exposure frequency	1.0	0.7	unitless
ED	Exposure duration	6.0	20	years
SIR	Soil ingestion rate	200	50	mg/day
AB1	Gastrointestinal absorption fraction	1.0	1.0	unitless
SA	Dermal surface area	2,200	2,500	cm ²
AF	Adherence factor	0.2	0.2	mg/cm ² -day
ABS_d	Dermal absorption fraction	See Note (1)	See Note (1)	unitless
CPF _o	Oral cancer potency factor	Chemical- specific	Chemical- specific	kg-day/mg
CPF_d	Dermal cancer potency factor	See Note (2)	See Note (2)	kg-day/mg
GI	Gastrointestinal absorption conversion factor	See Note (3)	See Note (3)	unitless

Notes:

(1) May use chemical-specific values or the following defaults: 0.01 for inorganic hazardous substances; 0.0005 for volatile organic compounds with vapor pressure ≥ benzene; 0.03 for volatile organic compounds with vapor pressure < benzene; 0.1 for other hazardous substances. See Appendix B.

- (2) Derived by $CPF_o \div GI$ (see Note 3).
- (3) May use chemical-specific values or the following defaults: 0.2 for inorganic hazardous substances; 0.8 for volatile organic compounds; 0.5 for other organic hazardous substances. See Appendix B.

Appendix D: Equations and Default Values for Calculating Potable Groundwater Cleanup Levels

Equation 720-1 (WAC 173-340-720^{xvii}): Potable Groundwater Cleanup Levels – Noncarcinogens

$$Potable \ Groundwater \ Cleanup \ Level \ (\mu g/L) = \frac{RfD_o \times ABW \times UCF \times HQ \times AT}{DWIR \times INH \times DWF \times ED}$$

Parameter	Definition	Default Value Method B	Default Value Method C	Units
RfD_o	Oral reference dose	Chemical-specific	Chemical-specific	mg/kg-day
ABW	Average body weight over the exposure duration	16	70	kg
UCF	Unit conversion factor	1,000	1,000	ug/mg
HQ	Hazard quotient	1.0	1.0	unitless
AT	Averaging time	6	6	years
DWIR	Drinking water ingestion rate	1.0	2.0	L/day
INH	Inhalation correction factor (1)	Chemical-specific (1)	Chemical-specific (1)	unitless
DWF	Drinking water fraction	1.0	1.0	unitless
ED	Exposure duration	6	6	years

Note:

(1) Use value of 2 for volatile organic compounds and 1 for all other substances. See Appendix B.

Equation 720-2 (WAC 173-340-720): Potable Groundwater Cleanup Levels – Carcinogens

Equation 720-2 (<u>WAC 173-340-720</u>^{xvii}): Potable Groundwater Cleanup Levels – Carcinogens

$$Potable \ Groundater \ Cleanup \ Level \ (\mu g/L) = \frac{RISK \times ABW \times AT \times UCF}{CPF_o \times DWIR \times ED \times INH \times DWF}$$

Parameter	Definition	Default Value Method B	Default Value Method C	Units
RISK	Acceptable cancer risk level	1.0E-6	1.0E-5	unitless
ABW	Average body weight over the exposure duration	70	70	kg
AT	Averaging time	75	75	years
UCF	Unit conversion factor	1,000	1,000	ug/mg
CPF _o	Oral carcinogenic potency factor	Chemical- specific	Chemical- specific	kg-day/mg
DWIR	Drinking water ingestion rate	2.0	2.0	L/day
INH	Inhalation correction factor	Chemical- specific (1)	Chemical- specific (1)	unitless
DWF	Drinking water fraction	1.0	1.0	unitless
ED	Exposure duration	30	30	years

Note:

(1) Use value of 2 for volatile organic compounds and 1 for all other substances. See Appendix B **Equation 720-3** (<u>WAC 173-340-720</u>xvii): Potable Groundwater Cleanup Levels – Petroleum Mixtures (Noncarcinogenic Effects)

$$C_{w} = \frac{HI \times AT}{\left[\frac{DWIR \times DWF \times ED}{ABW \times UCF}\right] \times \sum_{i=1}^{n} \frac{F_{(i)} \times INH_{(i)}}{RfD_{o_{(i)}}}}$$

Parameter	Definition	Default Value Method B	Default Value Method C	Units
C_w	TPH groundwater cleanup level	(calculated)	(calculated)	μg/L
HI	Hazard index	1.0	1.0	unitless
AT	Averaging time	6	6	years
DWIR	Drinking water ingestion rate	1.0	2.0	L/day
DWF	Drinking water fraction	1.0	1.0	unitless
ED	Exposure duration	6	6	years
ABW	Average body weight over the exposure duration	16	70	kg
UCF	Unit conversion factor	1,000	1,000	ug/mg
$F_{(i)}$	Fraction (by weight) of petroleum component (i)	Chemical- specific	Chemical- specific	unitless
$INH_{(i)}$	Inhalation correction factor for petroleum component (i)	Chemical- specific (1)	Chemical- specific (1)	unitless
$RfD_{o(i)}$	Oral reference dose of petroleum component (i)	Chemical- specific	Chemical- specific	mg/kg-day
n	The number of petroleum components (petroleum fractions plus volatile organic compounds with an <i>RfD_o</i>) present in the petroleum mixture (See Table 830-1.)	Mixture-specific	Mixture-specific	unitless

Note:

(1) Use value of 2 for volatile organic compounds and 1 for all other substances. See Appendix B.

Endnotes

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<sup>i</sup> https://apps.ecology.wa.gov/publications/summarypages/2509201.html
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https://fortress.wa.gov/ecy/ezshare/tcp/CLARC/ToxicityChemPropPetroleumMixtures.pdf

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- xiv https://app.leg.wa.gov/WAC/default.aspx?cite=173-340-740
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^{*} https://ecology.wa.gov/about-us/contact-us

xi https://app.leg.wa.gov/WAC/default.aspx?cite=173-340

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