



Guidance for Silica Gel Cleanup in Washington State

Toxics Cleanup Program

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Related Publications:

- Guidance for Remediation of Petroleum Contaminated Sites (Publication No. 10-09-057) at: <https://apps.ecology.wa.gov/publications/SummaryPages/1009057.html>
- Analytical Methods for Petroleum Hydrocarbons (Publication No. 97-602) at: <https://apps.ecology.wa.gov/publications/SummaryPages/97602.html>
- User's Manual: Natural Attenuation Analysis Tool Package for Petroleum-Contaminated Ground Water (Publication No. 05-09-091A) at: <https://apps.ecology.wa.gov/publications/SummaryPages/0509091A.html>

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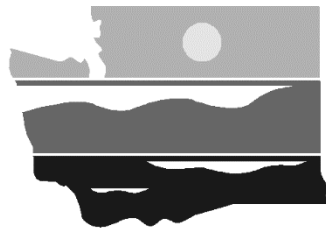
Southwest Region 360-407-6300	Northwest Region 206-594-0000	Central Region 509-575-2490	Eastern Region 509-329-3400
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DEPARTMENT OF
ECOLOGY
State of Washington

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Acronyms & Abbreviations

Acronym or Abbreviation	Definitions
µg/L	Micrograms per liter
CUL	Cleanup level
DRO	Diesel range organics
Ecology	Washington State Department of Ecology
EPA	Environmental Protection Agency
GRO	Gasoline range organics
IRIS	Integrated Risk Information System
MTCA	Model Toxics Control Act
NAPL	Non-aqueous phase liquid
NWTPH-Dx	A qualitative and quantitative method (extended) for semi-volatile (“diesel”) petroleum products in soil and water. Petroleum products applicable for this include jet fuels, kerosene, diesel oils, hydraulic fluids, mineral oils, lubricating oils, and fuel oils.
NWTPH-Gx	A qualitative and quantitative method (extended) for volatile (“gasoline”) petroleum products in soil and water. Petroleum products applicable for this method include aviation and automotive gasolines, mineral spirits, Stoddard solvent and naphtha.
NWTPH-HCID	Northwest TPH Hydrocarbon Identification
ORO	Oil range organics
PCL	Protective concentration level
PPRTV	Provisional Peer-Reviewed Toxicity Value
RfD	Reference dose
RSL	Regional screening level
SF-RWQCB	San Francisco Bay Regional Water Quality Control Board
SGC	Silica gel cleanup
TCEQ	Texas Commission of Environmental Quality
TOC	Total Organic Carbon
TPH	Total petroleum hydrocarbons

Chapter 1

1.0 Introduction

This guidance document provides details on the use of silica gel cleanup (SGC) in analyzing diesel and heavy oil range organics when using the Washington State Department of Ecology's (Ecology) NWTPH-Dx analytical method (see Ecology, 1997²) for petroleum hydrocarbons at a cleanup site regulated under the Model Toxics Control Act (MTCA) Regulation, Chapter 173-340 WAC.

The NWTPH method quantifies both petroleum compounds and non-petroleum polar organic compounds. Non-petroleum polar metabolites are discussed in Section 2.1. There are several potential sources of other non-petroleum polar organic compounds in weathered petroleum mixtures. These are discussed in Section 2.2.

Using SGC as part of the NWTPH-Dx analysis will help quantify the proportion of petroleum hydrocarbons to non-petroleum polar organics (which includes polar metabolites) in soil and groundwater samples and will help inform remedy decisions and groundwater monitoring timeframes.

What is Silica Gel Cleanup (SGC)?

SGC refers to a sample cleanup step in the analytical process where silica gel is used. Silica gel is a polar material that is used to adsorb (i.e., remove or cleanup) non-hydrocarbon polar organics during the sample extraction process.

Additional information on SGC can be found on the Interstate Technology and Regulatory Council's (ITRC's) [TPH Risk Evaluation at Petroleum-Contaminated Sites³ website](#) (See Section 3.3.3 and [Appendix A.3 Fact Sheet](#))

² The silica gel cleanup and separation technique under the NWTPH-Dx method is discussed on Page 23 of Ecology's 1997 publication: *Analytical Methods for Petroleum Hydrocarbons*. Publication No. ECY 97-602. June 1997 (Ecology, 1997). <https://apps.ecology.wa.gov/publications/SummaryPages/97602.html>

³ <https://tphrisk-1.itrcweb.org/>

Chapter 2

2.0 Background

Groundwater and soil samples are routinely collected and analyzed for total petroleum hydrocarbons (TPH), which include gasoline range organics (GRO), diesel range organics (DRO), and heavy oil range organics (ORO). The NWTPH-Dx method covers the quantitative analysis of semivolatile petroleum products including diesel fuels and heavy oils, and results in a single TPH value that can be used for comparison to Method A cleanup levels⁴ (Ecology, 1997). However, if DRO and ORO are reported separately by the laboratory, the results should be summed for comparison with Method A cleanup levels.

Note:

The preferred approach is to request the laboratory to report the entire DRO and ORO range together as one result, which avoids the possibility of double-counting fractions that are reported in both the DRO and ORO ranges.

Guidance on evaluating compliance when laboratories report separate DRO and ORO values is provided in Section 7.3 of Ecology's 2016 [Guidance for Remediation of Petroleum Contaminated Sites](#)⁵ and in Ecology's 2004 [Implementation Memorandum #4](#)⁶ (Ecology, 2004; Ecology, 2016).

2.1 Weathering and Polar Metabolites

Petroleum in groundwater may be dissolved, present as non-aqueous phase liquid (NAPL), or sorbed to particulate matter within the water matrix (e.g., colloids). Over time, petroleum dissolved in groundwater becomes weathered through processes that include microbial biodegradation, adsorption to soil particles, volatilization, and dissolution or leaching (Lang et al., 2009; SF-RWQCB, 2016). Biodegradation of petroleum in groundwater via microbial oxidation plays a major role in the weathering process resulting in the creation of non-petroleum compounds that have oxygen in their molecular structures (Atlas, 1981; Zemo, 2003; Zemo, 2013). These are often referred to as oxygen-containing polar compounds or polar metabolites (Zemo, 2013). Due to their overall greater solubility, polar metabolites such as organic acids/esters, alcohols, ketones, aldehydes, and phenols may constitute most of the contaminant mass in weathered petroleum groundwater plumes (Zemo, 2013; SF-RWQCB, 2016).

Petroleum hydrocarbons contain carbon and hydrogen and are non-polar in molecular structure (Zemo, 2003). On the other hand, polar metabolites have carbon, hydrogen, and oxygen, are

⁴ Ecology's Method A TPH values were derived using the entire range of TPH fractions present in each type of product, not based on splitting the test results between DRO and ORO (Ecology, 2016).

⁵ <https://apps.ecology.wa.gov/publications/SummaryPages/1009057.html>

⁶ <https://apps.ecology.wa.gov/publications/SummaryPages/0409086.html>

polar in molecular structure, are more soluble in water, and are not petroleum compounds (O'Reilly et. al., 2019; Zemo, 2003). As petroleum biodegrades in groundwater and moves away from the source, the percentage of polar metabolites tends to increase, and the toxicity of the overall mixture tends to decrease (Zemo, 2017).

2.2 Other Sources of Polar Organic Compounds

There are several potential sources of polar organic compounds in weathered petroleum mixtures. In addition to the polar metabolites discussed above, there can be organic compounds from naturally occurring organic matter (such as peat, leaf litter, bark, humic acids), also called biogenic interference (Ecology, 2016; Lundegard, et. al., 2004; ITRC, 2018). There may also be polar organic compounds contained in crude oils (e.g., compounds with nitrogen, sulfur, or oxygen) or other non-petroleum related organic chemicals such as pesticides and phthalates (Mohler et. al., 2013; SF-RWQCB, 2016). Use of SGC can help to reduce or eliminate any of these non-petroleum polar organics that may be in the sample (Ecology, 1997; Ecology, 2016).

2.3 NWTPH-Dx Analytical Method

The extraction and quantitative methods included in Ecology's NWTPH-Dx analysis are not specific to petroleum hydrocarbons, and what is measured includes both non-polar hydrocarbons and non-hydrocarbon polar organics potentially present from any of the sources discussed above. To address potential biogenic interference from non-hydrocarbon polar organics with the quantification of petroleum hydrocarbons in soil and groundwater, the NWTPH-Dx method includes a sample cleanup method (i.e., SGC) (Ecology, 1997). Using SGC in the sample extraction process removes the non-hydrocarbon polar organics (including polar metabolites) and what is measured in the cleaned-up extract are the petroleum hydrocarbons.

Notes:

(1) Use of SGC as part of the NWTPH-Dx Method. The SGC cleanup procedure is not used as a default to the NWTPH-Dx method. Rather, the NWTPH-Dx method specifies that SGC may be used to clean up the sample in cases where there may be potential interference from non-petroleum based naturally occurring organics (i.e., biogenic interferences) (Ecology, 1997). There should be coordination between the party conducting the sampling and the laboratory regarding the use of SGC as part of the NWTPH-Dx method. Reports that document NWTPH-Dx results should be clear on whether the results reflect the whole mixture (i.e., petroleum hydrocarbons and non-hydrocarbon polar organics) or just the petroleum hydrocarbons in the cleaned-up extract (using SGC).

(2) Use of sulfuric acid. Ecology no longer recommends using concentrated sulfuric acid for analysis with SGC; see discussion in Chapter 4.

Chapter 3

3.0 Use of SGC at MTCA Sites

You may use SGC as part of the NWTPH-Dx method when analyzing samples collected from sites with petroleum releases to soil or groundwater. SGC CANNOT be performed as part of the NWTPH-Gx method to quantify GRO because the cleanup step could result in loss of volatiles.

3.1 Soil Samples

Because most soils contain naturally occurring organic matter, use of SGC for soil extracts being analyzed using the NWTPH-Dx method is generally acceptable⁷, and the results (e.g., combined DRO and ORO) may be compared to Method A TPH soil cleanup levels.

3.2 Groundwater Samples

Unlike soil, most groundwater does not contain significant levels of naturally occurring organic matter. As a result, polar metabolites from the weathering process may account for a significant portion of the polar organics measured as TPH in groundwater. Due to the weathering process and the potential presence of polar organics, NWTPH-Dx analysis in groundwater without SGC may provide results that overestimate the portion of the sample consisting of petroleum hydrocarbons. At cleanup sites, a better understanding of the TPH composition (i.e., non-polar petroleum hydrocarbons vs polar organics) may help to:

- Determine if diesel and oil range organic mixtures in groundwater at the site are weathered and if there is evidence of natural attenuation⁸.
- Determine if naturally occurring organics are a significant component of the TPH being detected in the groundwater samples (see Section 3.2.1 below).
- Shorten the timeframe of groundwater monitoring by reaching compliance more quickly. For example, on-going groundwater monitoring may not be necessary if representative groundwater sampling with and without SGC at a site shows that the cleanup levels presented in Section 3.2.2 are met.

⁷ Some soil types may be low in organic matter and therefore SGC may not be needed. The decision to use SGC for soil extracts should be made in coordination with the Ecology site manager.

⁸ See Ecology's 2005 [Guidance on Remediation of Petroleum-Contaminated Ground Water By Natural Attenuation](https://apps.ecology.wa.gov/publications/documents/0509091.pdf) for technical guidance on how to evaluate the feasibility and performance of alternatives that use natural attenuation to clean up petroleum contaminated groundwater.

Notes:

(1) Compliance evaluation if SGC is used. SGC may be used when testing DRO in groundwater using the NWTPH-Dx analytical method, and it no longer depends on showing biogenic interferences⁹. When using SGC to demonstrate compliance, you should analyze groundwater samples from permanent monitoring wells¹⁰ both with and without applying SGC. The difference in the analytical results provides a measure of the non-petroleum polar organics within the sample. When using SGC, the nature and extent of petroleum impacted groundwater at a site should include a characterization of both petroleum hydrocarbons and polar metabolites. Sources of polar organics have been discussed previously in Section 2.1 and 2.2.

(2) Compliance evaluation if SGC is not used. The use of SGC when testing DRO in groundwater using the NWTPH-Dx analytical method is optional. If SGC is not used, then the whole petroleum mixture (e.g., DRO + ORO + any Polar Metabolites) in groundwater, as determined by whole product testing using NWTPH-Dx, should be compared to the Method A TPH groundwater level for compliance.

(3) Potential adjustments for biodegradation. The biodegradation process for petroleum may contribute to a depletion of dissolved oxygen levels in the groundwater, resulting in a chemically “reducing” condition. Under this condition, naturally occurring metals in the aquifer matrix are biologically and chemically transformed into more soluble and toxic forms. This is common for metals such as arsenic, manganese and iron. As such, it may not be enough to reduce petroleum concentrations including polar metabolites to the levels identified in Tables 2 and 3 below (see Section 3.2.2). Any increased mobilization of dissolved metals as a result of the petroleum biodegradation process is required to be evaluated and addressed as part of the cleanup. See Chapter 8.9 (Step 9) of Ecology’s 2016 [Guidance for Remediation of Petroleum Contaminated Sites](#)¹¹.

3.2.1 Accounting for Naturally Occurring Organics

Characterizing the contribution from naturally occurring organics in groundwater to the TPH totals may be done by analyzing clean representative background samples (located hydraulically upgradient of contaminant sources and releases to the site) from permanent monitoring wells¹². Temporary well points and groundwater grab samples may not be used to

⁹ The decision to use SGC in combination with the NWTPH-Dx method when analyzing TPH in groundwater should be made in coordination with the Ecology site manager.

¹⁰ Permanent monitoring wells allow for multiple rounds of sampling to account for seasonal variation (i.e., wet and dry seasons).

¹¹ <https://apps.ecology.wa.gov/publications/SummaryPages/1009057.html>

¹² Instruct the lab to split each background groundwater sample and perform the NWTPH-Dx analysis with and without SGC. Also, sample using the NWTPH-Gx method if GRO is a contaminant at the site. This is needed to verify that there are no detectable petroleum concentrations in the upgradient background data.

establish whether naturally occurring organics are present in groundwater. Background data should account for seasonal variation and should not contain any measurable petroleum hydrocarbons¹³. In addition, background data should include quantification of total organic carbon (TOC) using an approved analytical method (e.g., EPA 9060A or Standard Method 5310), and a review of chromatograms (with and without SGC) for signatures indicating the potential presence of polar organics. Polar organic concentrations identified within and downgradient of the plume may be adjusted if the contribution from naturally occurring organics (if any) is determined from representative background wells. See the example below for how an adjustment may be made.

In the example provided in **Table 1** below, the polar organic contribution from naturally occurring organics, as determined by sampling upgradient background groundwater wells, is 200 µg/L. The background data did not contain any detectable petroleum concentrations (based on NWTPH-Gx and NWTPH-Dx with SGC). Site related data within the plume indicates a NWTPH-Dx concentration of 1,000 µg/L with no SGC, and 400 µg/L with SGC. Based on this, the polar organic concentration within the plume is estimated to be 600 µg/L. However, since 200 µg/L may be attributed to naturally occurring organics, the concentration of polar organics that may be site related (polar metabolites of petroleum) is adjusted downward to 400 µg/L. The adjusted concentration may be compared to the polar organic cleanup level of 500 µg/L (see Section 3.2.2) to determine compliance.

Table 1. Example of adjusting the polar organic concentration to account for naturally occurring organics.

TPH Analytical Method	Concentration (µg/L)
Site Plume Data NWTPH-Dx (<i>no SGC</i>) = Total TPH (petroleum + polar organic concentration)	1,000
Site Plume Data NWTPH-Dx (<i>with SGC</i>) = petroleum concentration	400
Background Data (Naturally Occurring Organics) NWTPH-Dx (<i>no SGC</i>) ¹ =	200
Adjustment Calc. [NWTPH-Dx (<i>no SGC</i>)] – [NWTPH-Dx (<i>with SGC</i>)] – [Background NWTPH-Dx (<i>no SGC</i>)] = 1,000 – 400 – 200 polar organic concentration ²	400

Table Notes:

- ¹ Background NWTPH-Dx data with SGC should be non-detect at the practical quantitation limit (PQL) of 250 µg/L. (see Table 7.3 of [Ecology, 2016](#)). Use the lowest technically feasible PQL (in coordination with the Ecology site manager) if site-specific conditions (e.g., from matrix interference) contribute to elevated PQLs greater than 250 µg/L.

¹³ TPH results for GRO in groundwater should be non-detect using the NWTPH-Gx method, and DRO/ORO should be non-detect when the NWTPH-Dx method is used in combination with SGC.

- ² Without adjustment for background the polar organic concentration is 600 µg/L. However, since 200 µg/L may be attributed to naturally occurring organics, the concentration of polar organics that may be site related is 400 µg/L.

Note:

Determining if naturally occurring organics in groundwater are influencing the TPH concentration is an optional step and not a requirement for using SGC in site groundwater samples.

3.2.2 Groundwater Screening and Compliance

A substantial amount of study has been conducted by Zemo, et al. (2017) to characterize the chemical structure and potential toxicity of polar metabolites measured as DRO in groundwater sample extracts at biodegrading fuel impacted sites. Data from these studies have been used to derive drinking water cleanup levels for polar metabolites in groundwater (see **Appendix A**). As described below, polar metabolite groundwater cleanup levels were developed separately for sites that have detectable petroleum concentrations in groundwater, and for sites that do not.

Sites with Detectable Petroleum Hydrocarbons

TPH groundwater levels measured using the NWTPH-Dx method without SGC may be as high 1,000 µg/L if it is shown that both portions of the TPH mixture (i.e., petroleum and polar organics) are less than or equal to 500 µg/L. The cleanup levels in **Table 2** below should be used to demonstrate compliance using the NWTPH-Dx analytical method for sites that have detectable concentrations of petroleum hydrocarbons (i.e., detections using either NWTPH-Gx or -Dx with SGC).

Note:

For this scenario, the 500 µg/L cleanup level for polar organics applies throughout the entire site for compliance purposes, regardless of biodegradation stage (i.e., Stages 1 through 4; see **Appendix A**).

Table 2. Application of the polar metabolite cleanup level at sites with detectable concentrations of petroleum hydrocarbons

TPH Analytical Method	Concentration (µg/L)
NWTPH-Dx (<i>with SGC</i>) = petroleum concentration ¹	≤500 (petroleum cleanup level)
[NWTPH-Dx (<i>no SGC</i>)] – [NWTPH-Dx (<i>with SGC</i>)] = polar organic concentration	≤500 (polar metabolite cleanup level)

Table Note:

- ¹ The value of 500 µg/L for petroleum is referenced in WAC 173-340-900 Table 720-1 Method A Cleanup Levels for Groundwater (DRO + Oil: Total ≤ 500 µg/L; see Ecology 2016 Chapter 7.3 for evaluating results reported separately as diesel and oil).

For each individual groundwater sample you collect, instruct the lab to split the sample and perform the NWTPH-Dx analysis with and without SGC. Subtract the with SGC NWTPH-Dx result from the no SGC NWTPH-Dx result. Do this for each individual paired result. The difference between the two results (no SGC *minus* with SGC) is the polar organic concentration.

Notes:

(1) Use of Method A Cleanup Levels. If Method A is used to develop groundwater TPH cleanup levels, then whole product analysis using the NWTPH-Gx and/or NWTPH-Dx methods should be used to determine the TPH concentrations in groundwater at the site. Concentrations in groundwater for the individual TPH components (e.g., GRO and DRO + ORO) at a site may be compared directly to their Method A TPH groundwater cleanup level for compliance. Any concentrations of polar compounds determined using the NWTPH-Dx method with and without SGC should be compared directly against the appropriate cleanup level for polar metabolites provided in this guidance. It is generally appropriate to apply the Method A TPH cleanup levels, including the cleanup level for polar metabolites, without consideration of additive effects for compliance purposes¹⁴.

(2) Sites with mixtures of GRO, DRO, and ORO. The NWTPH-Dx method with and without SGC may be used when detectable concentrations of GRO, DRO, and ORO are present. The NWTPH-Dx method may be used to determine compliance with Method A TPH groundwater cleanup levels (i.e., for DRO, Heavy Oils, and Mineral Oil) and polar metabolites (via analysis with and without SGC). The NWTPH-Gx method (no SGC allowed) may be used to determine compliance with Method A TPH GRO groundwater cleanup levels. For sites where there is GRO in addition to DRO and/or ORO in groundwater, it's recommended that final compliance groundwater monitoring to demonstrate attainment of the groundwater cleanup standards for DRO/ORO plus polar metabolites wait until the GRO component is determined to be attenuated below its Method A cleanup level. This step is recommended to account for potential changes in groundwater concentrations (including any changes to the mass of polar metabolites) as a result of continued weathering of the groundwater plume. Final compliance monitoring should be conducted using the methods identified in this guidance for polar metabolites (if SGC is used) and consistent with Section 10.3 of Ecology, 2016.

(3) Sites with only GRO. If it can be confirmed that a site has only been impacted by a release of GRO and it's been determined that NWTPH-Dx testing is not required¹⁵, then a separate evaluation of polar metabolites may not be necessary. This is because the NWTPH-Gx method does not include the removal (via SGC) of non-petroleum polar organics that are either part of the product, or a by-product of biodegradation.

¹⁴ Site-specific Method B groundwater cleanup levels may be derived that account for additive effects of petroleum mixtures using a fractionation approach (see Section 8.9 of Ecology, 2016).

¹⁵ On a site-specific basis, if it's determined by the Ecology site manager that sampling via the NWTPH-Dx method is also warranted on a gasoline release site, then evaluation of polar metabolites should be conducted in accordance with the methods in this guidance. See Section 7.1 of Ecology 2016 on deciding which TPH products to test for.

Sites with No Detectable Petroleum Hydrocarbons

In this scenario, NWTPH-Gx and -Dx (with SGC) results should be non-detect (at a PQL of 250 µg/L¹⁶) throughout the site which indicates that there are no detectable concentrations of petroleum hydrocarbons. At these sites, TPH groundwater levels measured using the NWTPH-Dx method without SGC may be as high as 700 µg/L. The polar metabolite cleanup level in **Table 3** below may be used to demonstrate compliance under the NWTPH-Dx method for sites that have no detectable concentrations of petroleum hydrocarbons. This cleanup level applies throughout the entire site for compliance purposes, regardless of biodegradation stage (i.e., Stages 2 through 4; see **Appendix A**).

Note:

Stage 1, which is identified by the presence of dissolved petroleum, cannot be present to use the 700 µg/L polar metabolite cleanup level.

Table 3. Application of the polar metabolite cleanup level at sites with no detectable concentrations of petroleum hydrocarbons

TPH Analytical Method	Concentration (µg/L)
NWTPH-Dx (<i>no SGC</i>) = Total TPH (polar organic concentration)	≤700 (polar metabolite cleanup level)
NWTPH-Dx (<i>with SGC</i>) and NWTPH-Gx = petroleum concentration	Non-Detect at PQL of 250 anywhere on site ¹⁶

For each individual groundwater sample you collect, instruct the lab to split the sample and perform the NWTPH-Dx analysis with and without SGC. The NWTPH-Dx (with SGC) and any NWTPH-Gx results should be non-detect throughout the site which indicates that there are no detectable concentrations of dissolved hydrocarbons (i.e., Stage 1 is not present).

3.2.3 Considerations for Site-Specific Method B Groundwater Cleanup Levels

If Method B¹⁷ is used to develop a site-specific cleanup standard for groundwater, then fractionated product testing will be necessary using the extractable petroleum hydrocarbons (EPH) and/or volatile petroleum hydrocarbons (VPH) methods to determine the concentration of aliphatic and aromatic hydrocarbons in specific carbon ranges or fractions (Ecology, 2016). The

¹⁶ Use the lowest technically feasible PQL (in coordination with the Ecology site manager) if site-specific conditions (e.g., from matrix interference) contribute to elevated PQLs greater than 250 µg/L.

¹⁷ In the MTCATPH Workbook, Method C is only evaluated for soil direct contact exposure. Groundwater cleanup levels for ingestion of potable water are based on Method B only. Method C groundwater cleanup levels based on potable water ingestion may only be used at sites qualifying under the strict conditions set forth in [WAC 173-340-706\(1\)](#). Contact Ecology for methods to evaluate petroleum mixtures in groundwater that may qualify for a Method C groundwater cleanup level in accordance with [173-340-706\(1\)](#).

EPH method is used for semivolatile and non-volatile hydrocarbon fractions (e.g., DRO and ORO); the VPH method is used for volatile hydrocarbon fractions (e.g., GRO). Some petroleum mixtures contain both DRO/ORO and GRO ranges and need to be analyzed by both EPH and VPH.

The total TPH concentrations measured using the NWTPH-Gx and Dx methods will not necessarily equal the TPH concentrations measured using the EPH and VPH methods. This is because the different methods use different sample preparation methods and laboratory equipment to measure concentrations (Ecology, 2016). For example, the SGC cleanup procedure is not used as a default to the NWTPH-Dx method. However, because the use of SGC is an integral part of the EPH method, removal of non-petroleum polar organics that are either part of the product, or a by-product of biodegradation, cannot be avoided (Ecology, 2016). As a result, in contrast with the default NWTPH-Dx method, TPH concentrations measured using the EPH method do not account for the potential mass of non-petroleum polar metabolites that may be present in a weathered/biodegraded plume. These polar compounds may pose a risk to human health via the drinking water pathway and to aquatic receptors in the surface water.

When using EPH and VPH methods to derive a site-specific Method B groundwater cleanup level, the concentration of non-petroleum polar metabolites in groundwater at the site must also be evaluated utilizing the NWTPH-Dx method (with and without SGC).**

See the blue text box below.

*** If it can be definitively confirmed from the conceptual site model (CSM) that a site has only been impacted by a release of GRO, and it's been determined that EPH and NWTPH-Dx testing are not required¹⁸, then a separate evaluation of polar metabolites may not be necessary. This is because VPH and NWTPH-Gx methods do not include the removal (via SGC) of non-petroleum polar organics that are either part of the product, or a by-product of biodegradation. **Note:** Unless definitive information is available from the CSM, it is recommended that product types that may have been released at a site along with TPH analytical testing requirements be confirmed using the Northwest TPH Hydrocarbon Identification (NWTPH-HCID) method.*

¹⁸ On a site-specific basis, if it's determined by the Ecology site manager that sampling via EPH and NWTPH-Dx methods are also warranted on a gasoline release site, then evaluation of polar metabolites should be conducted in accordance with the methods in this guidance.

Use of EPH/VPH for Compliance in Groundwater

Compliance with Polar Metabolites. When conducting fractionated testing, it is recommended that whole product analysis using the NWTPH (NWTPH-Dx or Gx) methods also be conducted on split samples if compliance with polar metabolites has not already been established as discussed in Section 3.2.2 (Ecology, 2016)¹⁹. The split samples submitted for whole product analysis using the NWTPH-Dx method should be analyzed both with and without SGC to determine compliance with the appropriate polar metabolite cleanup level as discussed in Section 3.2.2.

Compliance with Petroleum Hydrocarbons. Whole product testing results using the NWTPH method (NWTPH-Dx or Gx) may also be used along with EPH/VPH results to determine compliance with Method B or C groundwater site-specific TPH cleanup levels. Table 10.1 of Ecology's [Guidance for Remediation of Petroleum Contaminated Sites](#)²⁰ explains alternative methods for evaluating confirmational monitoring data to determine if a site-specific TPH cleanup level derived using EPH/VPH has been met. Although Table 10.1 is specific to soil cleanup levels, it may also be applied to groundwater cleanup levels. Recommendations for application of SGC with regard to the alternatives provided in Table 10.1 are provided below.

Alternative 1:** The NWTPH-Dx method with SGC may be used to compare directly with the TPH cleanup level calculated using EPH/VPH data²¹.

Alternative 2:** This alternative requires the development of a good correlation between NWTPH and EPH/VPH analyses. This correlation may be based on NWTPH data with or without SGC.

Alternative 3:** This alternative is used when new site-specific TPH cleanup levels need to be calculated to account for situations where treatment methods change the composition of the TPH mixture. Under this alternative, confirmation sampling must be analyzed using the EPH/VPH methods.

** Each of the alternatives listed above should also include analysis via the NWTPH-Dx method both with and without SGC if compliance with polar metabolites has not already been established as discussed in Section 3.2.2.

¹⁹ See Section 7.1 (Step 2) of Ecology's 2016 [Guidance for Remediation of Petroleum Contaminated Sites](#).

²⁰ <https://apps.ecology.wa.gov/publications/SummaryPages/1009057.html>

²¹ You may also use the NWTPH-Dx result without SGC (a more conservative approach) to compare directly with the TPH cleanup level calculated using EPH/VPH data.

3.2.4 Considerations for Remediation

Biodegradation of contaminants from the use of groundwater remediation technologies such as air sparging can produce polar metabolites and/or cause impacts to polar metabolite plumes (e.g., inducing migration of the plume). Potential impacts to polar metabolite plumes from petroleum releases should be evaluated when selecting groundwater remediation technologies at a site.

3.3 Surface Water Protection

Aquatic Life Protection

Ecology's [Implementation Memo 23](#)²² provides GRO and DRO cleanup levels that are protective of aquatic receptors in marine and fresh surface waters (Ecology, 2021). DRO protective values are provided for both “Unweathered” and “Weathered” petroleum mixtures and were developed using the NWTPH-Dx method without SGC. As such, NWTPH-Dx results without SGC should be used to compare to the fresh and marine surface water cleanup levels for aquatic receptors for compliance purposes. However, one could use NWTPH-Dx results with and without SGC to identify which DRO cleanup level is most appropriate for the site (“Unweathered” or “Weathered²³”).

Human Health Protection

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 [Table 720-1](#)) as the Method B surface water level (in lieu of using [Equation 730-1](#)). See [WAC 173-340-730\(3\)\(b\)\(iii\)\(C\)](#). NWTPH-Dx analysis with and without SGC may be used to compare against the Method A TPH and polar metabolite groundwater levels as discussed in Section 3.2.

²² <https://apps.ecology.wa.gov/publications/SummaryPages/1909043.html>

²³ A “Weathered” plume will generally have a significant cleanup using silica gel.

Chapter 4

4.0 Updates to Existing Guidance

This guidance is intended to be used in conjunction with Ecology's [Analytical Method for Petroleum Hydrocarbons](#), NWTPH-Dx (Ecology, 1997), with an important update. The NWTPH-Dx method directs the user to perform the analysis using SGC and sulfuric acid if the water sample contains biological material (Ecology, 1997). **Ecology no longer recommends using concentrated sulfuric acid for analysis with SGC**, as it may result in an unintended loss of petroleum hydrocarbon products in the sample, affecting the accuracy of the analysis of the sample. The NWTPH-Dx method is in the process of being updated and will address this issue. The updated method is anticipated to be available in early 2024.

References

- Atlas, R.M. 1981. *Microbial degradation of petroleum hydrocarbons: An environmental perspective*. Microbiological Reviews 45: 180–209.
- Ecology (Washington State Department of Ecology), 1997. *Analytical Methods for Petroleum Hydrocarbons*. Publication No. ECY 97-602. June 1997.
<https://apps.ecology.wa.gov/publications/SummaryPages/97602.html>
- Ecology, 2004. Implementation Memo #4. *Determining Compliance with Method A Cleanup Levels for Diesel and Heavy Oil*. June 2004.
<https://apps.ecology.wa.gov/publications/SummaryPages/0409086.html>
- Ecology, 2016. *Guidance for Remediation of Petroleum Contaminated Sites*. Publication No. ECY 10-09-057 (June 2016).
<https://apps.ecology.wa.gov/publications/SummaryPages/1009057.html>
- Ecology, 2021. *Concentrations of Gasoline and Diesel Range Organics Predicted to be Protective of Aquatic Receptors in Surface Waters*. Implementation Memorandum No. 23. August 24, 2021.
<https://apps.ecology.wa.gov/publications/SummaryPages/1909043.html>
- ITRC, 2018. *TPH Risk Evaluation at Petroleum-Contaminated Sites*. Washington, D.C.: Interstate Technology & Regulatory Council, TPH Risk Evaluation Team. https://tphrisk-1.itrcweb.org/5-conceptual-site-models-and-investigative-strategies/#5_10
- Lang et al., 2009. Lang, D. A., Bastow, T. P., Van Aarssen, B. G., Warton, B., Davis, G. B., and Johnston, C. D. *Polar Compounds from the Dissolution of Weathered Diesel*. Groundwater Monitoring & Remediation. 29(4), 85-93.
- Lundegard, et al., 2004. Lundegard, P. D. and Sweeney, R. E. *Total Petroleum Hydrocarbons in Groundwater—Evaluation of Nondissolved and Nonhydrocarbon Fractions*. Environmental Forensics. 5:85–95, 2004.
- Mohler et al., 2013. Mohler, R. E., O'Reilly, K. T., Zemo, D. A., Tiwary, A. K., Magaw, R. I., and Synowiec, K. A. *Non-Targeted Analysis of Petroleum Metabolites in Groundwater Using GC×GC–TOFMS*. Environmental Science & Technology. 2013, 47, 10471–10476.
- O'Reilly et al., 2019. O'Reilly, K. T., Mohler, R. E., Zemo, D. A., Ahn, S., Magaw, R. I., and Devine, C. E. *Oxygen-Containing Compounds Identified in Groundwater from Fuel Release Sites Using GC×GC–TOF-MS*. Groundwater Monitoring & Remediation. 39, no. 4/ Fall 2019/pages 32–40.
- SF-RWQCB, 2016. *Petroleum Metabolites Literature Review and Assessment Framework. Technical Resource Document*. San Francisco Bay Regional Water Quality Control Board. June 27, 2016.
- Zemo, et al., 2003. Zemo, D.A and Foote, G.R. *The Technical Case for Eliminating the Use of the TPH Analysis in Assessing and Regulating Dissolved Petroleum Hydrocarbons in Ground Water*. Groundwater Monitoring & Remediation. 23, no. 3/ Summer 2003/pages 95–104. <https://ngwa.onlinelibrary.wiley.com/doi/abs/10.1111/j.1745-6592.2003.tb00687.x>.
- Zemo, et al., 2013. Zemo, D.A, O'Reilly, K.T., Mohler, R.E., Tiwary, A.K., Magaw, R.I., and Synowiec, K. A. *Nature and Estimated Human Toxicity of Polar Metabolite Mixtures in Groundwater Quantified as TPHd/DRO at Biodegrading Fuel Release Sites*.

Groundwater Monitoring & Remediation. 33, no. 4/ Fall 2013/pages 44–56.
<https://ngwa.onlinelibrary.wiley.com/doi/full/10.1111/gwmr.12030>

Zemo, et al., 2017. Zemo, D.A, O'Reilly, K.T., Mohler, R.E., Magaw, R.I., Devine, C.E., Ahn, S., and Tiwary, A.K. *Life Cycle of Petroleum Biodegradation Metabolite Plumes, and Implications for Risk Management at Fuel Release Sites*. Integrated Environmental Assessment and Management v13, n4: 714-727.
<https://setac.onlinelibrary.wiley.com/doi/pdf/10.1002/ieam.1848>

Appendix A: Polar Metabolite Toxicity and Cleanup Level

A-1 Introduction

A substantial amount of study has been conducted by Zemo, et al. (2017), to characterize the chemical structure and potential toxicity of metabolites measured as diesel range organics (DRO) in groundwater sample extracts at biodegrading fuel impacted sites. The study included collecting 83 groundwater samples from 16 fuel terminal sites and five gas stations between 2011 and 2015. Samples were evaluated using: 1) a targeted analysis of 76 potential polar metabolite compounds (via EPA Method 8270C); and 2) a non-targeted qualitative approach (via full-scan mode) to tentatively identify additional polar metabolites.

The targeted list of 76 compounds consists of potential polar metabolites with agency-derived oral reference doses (RfDs) and additional compounds with toxicity information, but no agency derived RfDs. Findings from the study have helped inform the human health toxicity of the polar metabolites. This appendix summarizes the study results.

A-2 Biochemistry of Petroleum Biodegradation

A key study element involved researching the literature to better understand the biodegradation pathways for refined petroleum fuels (e.g., diesel). This research resulted in the identification of five families and 22 structural classes of polar metabolites that are expected to result from the aerobic and anaerobic biodegradation of petroleum (see **Table A-3**²⁴).

A-3 Human Health Toxicity of Metabolite Structural Classes

The study identified representative compounds or classes of compounds (e.g., C6-C22 n-alkyl carboxylic acids) for each of the 22 structural classes and included a toxicity assessment. Researchers reviewed human-health criteria (i.e., RfD) and obtained data from regulatory databases (in 2012): 1) [EPA's Regional Screening Levels \(RSLs\)](#)²⁵; and 2) the [Texas Commission on Environmental Quality \(TCEQ\) Protective Concentration Levels \(PCLs\)](#)²⁶. Both databases use [EPA's Integrated Risk Information System \(IRIS\)](#)²⁷ as the preferred source of toxicity data. The toxicity assessment was expanded to include representative compounds, or classes of compounds, with toxicity information associated with the various structural classes (e.g., no observed adverse effect levels) but not agency derived RfDs.

²⁴ Table A-3 is located at the end of Appendix A.

²⁵ <https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables>

²⁶ <https://www.tceq.texas.gov/remediation/trrp/trrppcls.html>

²⁷ <https://www.epa.gov/iris>

The toxicity assessment resulted in the identification of chronic oral RfDs for the representative compounds identified for each structural class. This information was used to assign an overall toxicity ranking for each structural class. The toxicity rankings are summarized below.

- Low – RfD \geq 0.1 mg/kg/day.
- Low to moderate – RfD \geq 0.01 to $<$ 0.1 mg/kg/day.
- Moderate – RfD \geq 0.001 to $<$ 0.01 to mg/kg/day.

Table A-3 at the end of this appendix lists the toxicity rankings for each of the 22 structural classes.

Ecology compared the toxicity values from 2012 with more recent values from 2023. This included a review of our [Cleanup Levels and Risk Calculation \(CLARC\)](#)²⁸ database from January 2023, EPA's fall 2022 RSL table (EPA, 2022), and TCEQ's March 2023, PCL table (TCEQ, 2023). This review resulted in two potential changes in the toxicity ranking as discussed below.

- **Polycyclic Aromatic Ketone Structural Class** – Benzophenone is a polycyclic aromatic ketone with a published oral RfD of 0.0067 mg/kg-day. This represents a moderate toxicity value, since the RfD is less than 0.01. However, this compound was not detected as part of the targeted analysis, and the toxicity ranking for this class remains low to moderate.
- **(N- and Alkyl) Alcohols** – 2-Ethyl-1-hexanol is an alkyl alcohol that has published oral RfDs from EPA (0.07 mg/kg-day) and TCEQ (0.15 mg/kg-day). EPA's Provisional Peer-Reviewed Toxicity Values Toxicity Value (PPRTV) of 0.07 mg/kg-day was published in 2019 and represents a low to moderate toxicity value. However, all the representative chemicals that makeup the (n- and alkyl) alcohols structural class, with the exception of 2-Ethyl-1-hexanol, are classified as low toxicity. Because EPA's PPRTV is only slightly lower than 0.1 mg/kg-day (the threshold for low toxicity), and the fact that all the other representative chemicals in this class are low toxicity, the toxicity ranking for this class remains at low.

A-4 Analytical Results

76 Targeted Compounds

Out of the 76 targeted metabolite compounds, eight were detected, based on groundwater samples that did not contain separate-phase product. These included four acids/esters, three

²⁸ <https://ecology.wa.gov/Regulations-Permits/Guidance-technical-assistance/Contamination-clean-up-tools/CLARC>

alcohols, and one ketone. Dodecanoic acid had the most detects at 18. The other seven compounds had three or fewer detects. Compounds identified as aldehydes and phenols were not detected.

Non-Targeted qualitative/full scan

Due to the relatively few detections in the targeted compound results, the non-targeted qualitative full-scan results were used to derive the per-sample average percentile for each polar family and structural class, and by biodegradation stage (see **Table A-3** and **Figure A-1**). The unique polar metabolites tentatively identified in each sample using the non-targeted full-scan approach were categorized into their respective polar families, structural classes, and associated toxicity ranking. For each sample within a particular biodegradation stage, the metabolites identified were calculated as a percentage by dividing the total number of identified compounds in each molecular family/structural class by the total number of identified metabolites in that sample. Results for each biodegradation stage, as illustrated in **Figure A-1**, are discussed below. The average toxicity of the metabolite mixture decreases with each progressive stage. That is, the percentage of the mixture identified as low toxicity increases.

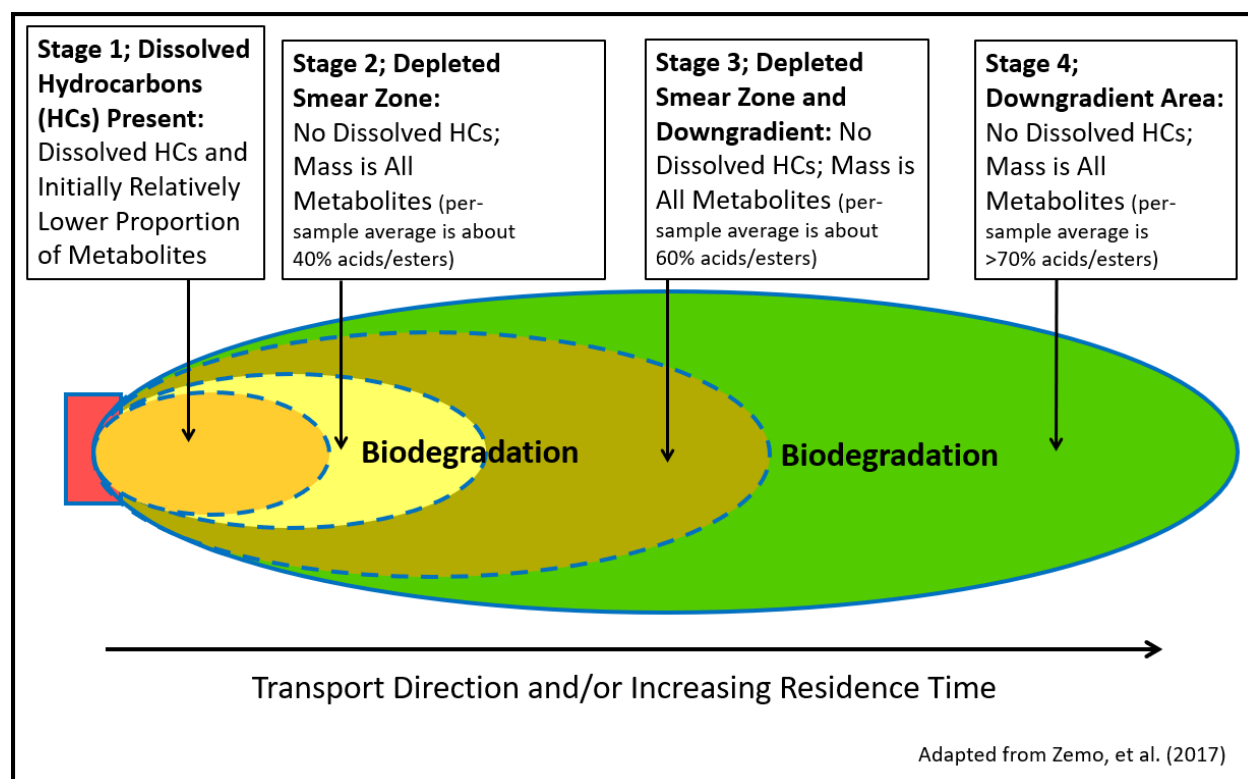


Figure A-1: Conceptual model of a weathered groundwater diesel-range organic plume.

- Stage 1** – This stage is identified by the presence of dissolved hydrocarbons in the source area and in downgradient groundwater. The metabolite mixture consists mainly of alcohols and ketones (36% alcohols: 32% ketones). Acids/esters account for approximately 21%. Aldehydes and phenols account for only 10%. The total average toxicity of the mixture is 78% low, 20% low to moderate, and 2% moderate.

- **Stage 2** – This stage is identified by the lack of dissolved hydrocarbons. However, samples are within the depleted smear zone, where residual TPH is present in smear zone soil. The metabolite mixture consists mainly of acids/esters (42%), and alcohols and ketones account for 26% and 25%, respectively. Aldehydes and phenols account for only 8%. The total average toxicity of the mixture 81% low, 19% low to moderate, and 0% moderate.
- **Stages 3 and 4** – Both of these stages are characterized by a lack of dissolved hydrocarbons. Stage 3 combines data from the Stage 2 depleted smear zone with data from the Stage 4 downgradient area that is outside the depleted smear zone. Stage 4 consists of only the downgradient area outside the depleted smear zone. The metabolite mixture of these stages consists mainly of acids/esters (64% Stage 3; 75% Stage 4) and alcohols (19% Stage 3; 16% Stage 4). The total average toxicity of the mixture for Stage 3 is 90% low, 10% low to moderate, and 0% moderate. The total average toxicity of the mixture for Stage 4 is 95% low, 5% low to moderate, and 0% moderate.

A-5 Polar Metabolite Cleanup Level

A conservative approach to developing a polar metabolite screening level is to apply the low end of the range of RfDs (i.e., high end of the toxicity range) to the percent composition identified for each polar family/class as identified in **Table A-3**. The low end of the oral RfD range is identified as follows: 0.1 mg/kg-day represents low toxicity, 0.01 mg/kg-day represents low to moderate toxicity, and 0.001 mg/kg-day represents moderate toxicity. As an example, using **Table A-3** data, the Stage 1 metabolite mixture consists of 78% at an oral RfD of 0.1 mg/kg-day, 20% at 0.01 mg/kg-day, and 2% at 0.001 mg/kg-day. With few exceptions, this approach applies the most conservative RfDs (i.e., lowest RfDs) resulting from the toxicity assessment for each polar family/class. Some exceptions are noted below. However, the compounds with exceptions were shown to be non-detect in the targeted analysis at a low reporting limit of generally 10 µg/L. It's noted that 2-ethyl-1-hexanol was not included for targeted analysis.

- **Alcohols (n- and alkyl)**

2-Ethyl-1-hexanol is an alkyl alcohol that has published oral RfDs from EPA (0.07 mg/kg-day) and TCEQ (0.15 mg/kg-day). EPA's PPRTV of 0.07 mg/kg-day was published in 2019 and represents a low to moderate toxicity value. However, all the representative chemicals that makeup the (n- and alkyl) alcohols structural class, with the exception of 2-ethyl-1-hexanol, are classified as low toxicity. Because EPA's PPRTV is only slightly lower than 0.1 mg/kg-day (the threshold for low toxicity), and the fact that all the other representative chemicals in this class are low toxicity, the toxicity ranking for this class remains at low.

- **Acids and Esters (n- and alkyl)**

Hexanoic acid has a low to moderate toxicity value but was not detected in any of the samples submitted for targeted analysis. All other compounds that make up this class have RfDs of 0.1 mg/kg-day or higher. Therefore, the class was assigned low toxicity.

- **Acids and Esters (Aromatic)**

Benzenedicarboxylic acid has a low to moderate toxicity value but was not detected in any of the samples submitted for targeted analysis. All other compounds that make up this class have RfDs of 0.1 mg/kg-day or higher. Therefore, the class was assigned low toxicity.

- **Ketones (n- and alkyl)**

2-Hexanone has a moderate toxicity value but was not detected in any of the samples submitted for targeted analysis. All other compounds that make up this class have RfDs of 0.01 mg/kg-day or higher. Therefore, the class was assigned low to moderate toxicity.

- **Ketones (Polycyclic aromatic)**

9,10-Anthraquinone and benzophenone have moderate toxicity values but were not detected in any of the samples submitted for targeted analysis. All other compounds that make up this class have RfDs of 0.01 mg/kg-day or higher. Therefore, the class was assigned low to moderate toxicity.

- **Phenols (non-C14 Alkyl phenols)**

2,6-Dimethylphenol has an RfD of 0.0006 mg/kg-day, which is less than the moderate toxicity range of ≥ 0.001 to < 0.01 mg/kg-day. However, this chemical was not detected in any samples submitted for targeted analysis. All other compounds that make up this class have RfDs of 0.001 mg/kg-day or higher. Therefore, the class was assigned moderate toxicity.

How were the polar metabolite cleanup levels determined?

Sites with Detectable Petroleum Hydrocarbons

The first two biodegradation stages (i.e., Stages 1 and 2) were used to develop a cleanup level for polar metabolites at sites that have detectable concentrations of dissolved petroleum hydrocarbons (i.e., detections using either NWTPH-Gx or -Dx with SGC). This cleanup level should be conservatively applied to all biodegradation stages at sites that still have dissolved hydrocarbons. To develop the cleanup level, weighted oral RfDs (units of mg/kg-day) were derived based on the total average toxicity of the mixture for Stages 1 and 2 using the formulas below along with the data in **Table A-3**.

$$\text{RfD weighted avg} = \frac{1}{\left(\frac{\% \text{ low}}{\text{low RfD}} + \frac{\% \text{ low to mod}}{\text{low to mod RfD}} + \frac{\% \text{ mod}}{\text{mod RfD}} \right)}$$

$$\text{Stage 1 RfD weighted avg} = \frac{1}{\left(\frac{78\%}{0.1} + \frac{20\%}{0.01} + \frac{2\%}{0.001} \right)} = 0.021 \text{ mg/kg-day}$$

$$\text{Stage 2 RfD weighted avg} = \frac{1}{\left(\frac{81\%}{0.1} + \frac{19\%}{0.01} + \frac{0\%}{0.001}\right)} = 0.037 \text{ mg/kg-day}$$

The weighted oral RfDs derived for Stages 1 and 2 as shown above result in drinking water cleanup levels (at two significant figures) of 340 µg/L for Stage 1 and 590 µg/L for Stage 2 (using Model Toxic Control Act [Equation 720-1](#)). Averaging Stage 1 and 2 results yields a polar metabolite cleanup level of 470 µg/L. This value is rounded up to 500 µg/L to represent an overall polar metabolite cleanup level that should be applied to all biodegradation stages (i.e., Stages 1 through 4) where petroleum hydrocarbons are still detected at the site.

Note:

For sites that have detectable concentrations of petroleum hydrocarbons, the polar metabolite cleanup level of 500 µg/L should be used throughout the entire site for compliance purposes, even if different biodegradation stages are present in different areas of the site.

Sites with No Detectable Petroleum Hydrocarbons

The second two biodegradation stages (i.e., Stages 2 and 3) were used to develop a cleanup level for polar metabolites at sites that have no detectable concentrations of petroleum hydrocarbons. This cleanup level should be conservatively applied to all biodegradation stages at sites that have no detectable concentrations of petroleum hydrocarbons (i.e., no detects using NWTPH-Gx or -Dx with SGC) at the practical quantitation limit (PQL) of 250 µg/L²⁹ (see Table 7.3 of Ecology, 2016). To develop the cleanup level, weighted oral RfDs (units of mg/kg-day) were derived based on the total average toxicity of the mixture for Stages 2 and 3 using the formulas below along with the data in **Table A-3**.

$$\text{RfD weighted avg} = \frac{1}{\left(\frac{\% \text{ low}}{\text{low RfD}} + \frac{\% \text{ low to mod}}{\text{low to mod RfD}} + \frac{\% \text{ mod}}{\text{mod RfD}}\right)}$$

$$\text{Stage 2 RfD weighted avg} = \frac{1}{\left(\frac{81\%}{0.1} + \frac{19\%}{0.01} + \frac{0\%}{0.001}\right)} = 0.037 \text{ mg/kg-day}$$

$$\text{Stage 3 RfD weighted avg} = \frac{1}{\left(\frac{90\%}{0.1} + \frac{10\%}{0.01} + \frac{0\%}{0.001}\right)} = 0.053 \text{ mg/kg-day}$$

The weighted oral RfDs derived for Stages 2 and 3 as shown above result in drinking water cleanup levels (at two significant figures) of 590 µg/L for Stage 2 and 850 µg/L for Stage 3 (using Model Toxic Control Act [Equation 720-1](#)). Averaging Stage 2 and 3 results yields a polar

²⁹ Use the lowest technically feasible PQL (in coordination with the Ecology site manager) if site-specific conditions (e.g., from matrix interference) contribute to elevated PQLs greater than 250 µg/L.

metabolite cleanup level of 720 µg/L. This value is rounded down to 700 µg/L to represent an overall polar metabolite protective level that can be applied to biodegradation Stages 2 through 4 where detectable concentrations of petroleum hydrocarbons are no longer present.

Note:

For sites that have no detectable concentrations of petroleum hydrocarbons (i.e., no detects using NWTPH-Gx or -Dx with SGC), the polar metabolite cleanup level of 700 µg/L should be used throughout the entire site for compliance purposes, even if different biodegradation stages are present in different areas of the site. Stage 1, which is identified by the presence of dissolved petroleum, cannot be present to use the 700 µg/L polar metabolite cleanup level.

Future updates to the polar metabolite cleanup levels

Ecology may update the drinking water cleanup levels and approach for screening polar metabolites as new toxicity information becomes available, including any new information on the composition of polar organics in weathered petroleum. However, in the interim, the polar metabolite cleanup levels established herein may be used to demonstrate human health protectiveness at a site.

A-6 Application of the Polar Metabolite Cleanup Level

Sites with Detectable Petroleum Hydrocarbons

TPH groundwater levels measured using the NWTPH-Dx method without SGC may be as high 1,000 µg/L if it is shown that both portions of the TPH mixture (i.e., petroleum and polar organics) are less than or equal to 500 µg/L. The cleanup levels in **Table A-1** below should be used to demonstrate compliance using the NWTPH-Dx analytical method for sites that have detectable concentrations of petroleum hydrocarbons (i.e., detections using either NWTPH-Gx or -Dx with SGC). **Note:** For this scenario, the 500 µg/L cleanup level for polar organics applies throughout the entire site for compliance purposes, regardless of biodegradation stage (i.e., Stages 1 through 4).

Table A-1. Application of the polar metabolite cleanup level at sites with detectable concentrations of petroleum hydrocarbons

TPH Analytical Method	Concentration (µg/L)
NWTPH-Dx (<i>with SGC</i>) = petroleum concentration ¹	≤500 (petroleum cleanup level)
[NWTPH-Dx (<i>no SGC</i>)] – [NWTPH-Dx (<i>with SGC</i>)] = polar organic concentration	≤500 (polar metabolite cleanup level)

Table Note:

¹ The value of 500 µg/L for petroleum is referenced in WAC 173-340-900 Table 720-1 Method A Cleanup Levels for Groundwater (DRO + Oil: Total ≤ 500 µg/L; see Ecology 2016 Chapter 7.3 for evaluating results reported separately as diesel and oil).

For each individual groundwater sample you collect, instruct the lab to split the sample and perform the NWTPH-Dx analysis with and without SGC. Subtract the with SGC NWTPH-Dx result from the no SGC NWTPH-Dx result. Do this for each individual paired result. The difference between the two results (no SGC *minus* with SGC) is the polar organic concentration.

Sites with No Detectable Petroleum Hydrocarbons

In this scenario, NWTPH-Gx and -Dx (with SGC) results should be non-detect (at a PQL of 250 µg/L³⁰) throughout the site which indicates that there are no detectable concentrations of petroleum hydrocarbons. At these sites, TPH groundwater levels measured using the NWTPH-Dx method without SGC may be as high as 700 µg/L. The polar metabolite cleanup level in **Table A-2** below should be used to demonstrate compliance under the NWTPH-Dx method for sites that have no detectable concentrations of petroleum hydrocarbons. This cleanup level applies throughout the entire site for compliance purposes, regardless of biodegradation stage (i.e., Stages 2 through 4). **Note:** Stage 1, which is identified by the presence of dissolved petroleum, cannot be present to use the 700 µg/L polar metabolite cleanup level.

Table A-2. Application of the polar metabolite cleanup level at sites with no detectable concentrations of petroleum hydrocarbons

TPH Analytical Method	Concentration (µg/L)
NWTPH-Dx (<i>no SGC</i>) = Total TPH (polar organic concentration)	≤700 (polar metabolite cleanup level)
NWTPH-Dx (<i>with SGC</i>) = petroleum concentration	Non-Detect at PQL of 250 anywhere on site ³⁰

For each individual groundwater sample you collect, instruct the lab to split the sample and perform the NWTPH-Dx analysis with and without SGC. The NWTPH-Dx (with SGC) and any NWTPH-Gx results should be non-detect throughout the site which indicates that there are no detectable concentrations of dissolved hydrocarbons (i.e., Stage 1 is not present).

³⁰ Use the lowest technically feasible PQL (in coordination with the Ecology site manager) if site-specific conditions (e.g., from matrix interference) contribute to elevated PQLs greater than 250 µg/L.

Appendix A References

EPA, 2022. *Regional Screening Levels (RSLs) - Generic Tables*. November 2022.

<https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables>

TCEQ, 2023. Current PCL Tables - Published March 2023.

<https://www.tceq.texas.gov/remediation/trrp/trrppcls.html>

Zemo, et. al., 2017. Zemo, D.A, O'Reilly, K.T., Mohler, R.E., Magaw, R.I., Devine, C.E., Ahn, S., and Tiwary, A.K. *Life Cycle of Petroleum Biodegradation Metabolite Plumes, and Implications for Risk Management at Fuel Release Sites*. Integrated Environmental Assessment and Management v13, n4: 714-727.

<https://setac.onlinelibrary.wiley.com/doi/pdf/10.1002/ieam.1848>

Table A-3: Summary of Structural Classes and Toxicity for “Biodegradation Stages” 1-4⁽¹⁾

Polar Family	Specific Structural Class	Expected Chronic Oral Toxicity for Humans ⁽³⁾	Biodegradation Stages ⁽²⁾			
			Stage 1	Stage 2	Stage 3	Stage 4
			Per-Sample Average (%) ⁽⁴⁾			
Alcohols (and diols)	n- and Alkyl alcohols	Low	20	11	9	8
	Cycloalkyl alcohols	Low	13	10	6	4
	Bicyclic alkyl alcohols	Low	1	3	3	3
	Aromatic alcohols	Low	2	2	1	1
	Polycyclic aromatic alcohols	Low to moderate	0	0	0	0
Totals			36	26	19	16
Acids (and esters)	n-and Alkyl acids/esters	Low	15	30	52	63
	Cycloalkyl acids/esters	Low	2	5	4	4
	Bicyclic alkyl acids/esters	Low	0	2	1	0
	Aromatic acids/esters	Low	4	5	7	8
	Polycyclic aromatic acids/esters	Low to moderate	0	0	0	0
Totals			21	42	64	75
Ketones	n-and Alkyl ketones	Low to moderate	10	8	5	3
	Cycloalkyl ketones	Low	15	7	3	1
	Bicyclic alkyl ketones	Low	3	6	2	1
	Aromatic ketones	Low to moderate	4	4	2	1
	Polycyclic aromatic ketones	Low to moderate	0	0	0	0
Totals			32	25	12	6
Aldehydes	n-and Alkyl aldehydes	Low to moderate	4	6	2	1
	Cycloalkyl aldehydes	Low to moderate	1	0	0	0
	Bicyclic alkyl aldehydes	Low to moderate	0	0	0	0
	Aromatic aldehydes	Low to moderate	2	1	0	0
	Polycyclic aromatic aldehydes	Low to moderate	0	0	0	0
Totals			7	7	2	1
Phenols	non-C14 Alkyl phenols	Moderate	2	0	0	0
	C14 Alkyl phenols ⁽⁵⁾	Low	1	1	0	1
	Phenol	Low	0	0	1	1
Totals			3	1	1	2
Total Avg Tox L/L-M/M⁽⁶⁾			78/20/2	81/19/0	90/10/0	95/5/0

Notes:

- Table modified from Zemo et al. (2017)
- Stage 1** = all Service Station samples (n=10); **Stage 2** = Terminals (Ts) 1-4 Source Area samples (n=14); **Stage 3** = Ts 1-4 Source Area and all Ts Downgradient Samples (n=44); **Stage 4** = All Ts Downgradient Samples (n=30).
- The approximate toxicity of each polar subclass is estimated based on toxicity data for individual chemicals within the subclass. Oral Reference Dose (RfD) in mg/kg/day. “Low”: RfDs ≥ 0.1 ; “Low to Moderate”: RfDs < 0.1 to 0.01 ; “Moderate”: RfDs < 0.01 to 0.001 .
- The per-sample average % data is based on the GC x GC non-targeted analyses. All groundwater samples without entrained separate-phase product collected between 2011 and 2015 were used.
- Where identified, 2,4- and 3,5- ditertbutylphenol (DTBP) are classified as alkylphenols but are assigned a Low toxicity ranking based on toxicity data for the di-substituted alkylphenol category from USEPA (2009).
- Total Avg Tox L/L-M/M = averages in percent for each toxicity classification for each Stage: “Low”/ “Low to Moderate”/ “Moderate”

Attachment A: Response to comments on the September 2022 review draft of *Guidance for Silica Gel Cleanup in Washington State*

A public comment period was held from September 13, 2022, through October 13, 2022, for the review draft of this document. The comments received during that period helped inform modifications made to the version of the document that was provided for public comment (dated September 2022) and are summarized below. Several editorial changes were also made to the review draft that are not reflected in this response to comments section.

General/Format/Editorial

1. (Ryan Hultgren) Appendix A contains Figure 2 and Appendix B contains Figure 3. Suggest having either Appendices A and B, and not the two figures listed separately, or Figures 2 and 3 and not the two appendices.

Add acronyms for gasoline range organics (GRO) and oil range organics (ORO). Should there be an acronym for polar metabolites?

µg/L = Micrograms per liter (use American spelling to be consistent).

Response: Appendix A and B have been removed along with Figures 2 and 3. Appendix C is now Appendix A. We have added GRO and ORO to the acronym list. We have changed the definition of µg/L to micrograms per liter.

2. (Landau Associates) Titles for Appendix A, B, and C are not provided, whereas the title for Appendix C is provided. Suggest providing the title for each appendix in the table of contents.

In reference to Appendix A: Inconsistencies/typos

- a. Ensure that the flow chart matches the logic outlined in the guidance document.
- b. Acronym list is incomplete and GRO is listed twice.
- c. Title at bottom of Figure has typo, “get” instead of “gel.”
- d. Diamond with “Are test results:” is missing the slash in the “w/.”

Response: Appendix A and B as originally provided have been removed. Appendix C is now Appendix A. Appendix A is titled: *Polar Metabolite Toxicity and Cleanup Level*. The flow chart referenced in Comment “a” has been removed. Comments “b to d” above have been addressed.

3. (Anonymous) The designation and numbering of appendices, tables and figures throughout the document does not follow standard convention (e.g., figures and tables should be specific to the appendix in which they are contained and not apply to other appendices or the document itself).

Response: The document has been updated and the format follows standard convention.

- (Ryan Hultgren) Sect 1. Add acronyms GRO and ORO.

Response: We have added GRO and ORO to the acronym list.

- (Ryan Hultgren) Define “SGC” in Section 2.0 instead of 3.0. Also, silica gel is used in preparing the sample for analysis not “used in the TPH analysis”. Suggested edit:

“Silica gel cleanup (SGC) can be used in preparing the sample for TPH analysis...”

Response: SGC is defined after its first occurrence in Section 1. We included this text to describe SGC: *SGC refers to a sample cleanup step in the analytical process where silica gel is used. Silica gel is a polar material that is used to adsorb (i.e., remove or cleanup) non-hydrocarbon polar organics during the sample extraction process.*

- (Manchester Lab) Will this guidance be updated based on the outcome of the NWTPH-Dx study by Will Hobbs (for Arthur Buchan), which is comparing silica gel cleanup methods?

Response: Updates to guidance are discussed in Section 4 which indicates that the NWTPH-Dx study is anticipated to be complete in early 2024. Section 4 will be updated as needed based on the finalization of NWTPH-Dx study.

TPH Analytics/Analytical Method

- (Scott Hooten – Port of Tacoma) Changes to the method for NWTPH-Dx analyses should be explained through the process of revising Analytical Methods for Petroleum Hydrocarbons (Pub. No. ECY 97-602). The draft Silica Gel Cleanup guidance includes a recommendation to not use concentrated sulfuric acid for NWTPH-Dx analyses and conflicts with the technical description in ECY 97- 602. The Port believes this conflict will create an unnecessary source of confusion amongst laboratories, consultants, regulators, and the regulated community until Pub. No. ECY 97- 602 is updated.

Response: This guidance is intended to be used in conjunction with Ecology’s Analytical Method for Petroleum Hydrocarbons, NWTPH-Dx (Ecology, 1997), with an important update. Ecology no longer recommends using concentrated sulfuric acid for analysis with SGC, as it may result in an unintended loss of petroleum hydrocarbon products in the sample, affecting the accuracy of the analysis of the sample. We recommend that you and your consultants communicate directly with the lab regarding not using concentrated sulfuric acid as part of the SGC under NWTPH-Dx. The NWTPH-Dx method is in the process of being updated and will address this issue. The updated method is anticipated to be available in early 2024.

- (Ryan Hultgren) It appears there may be two Ecology projects being conducted related to the use of SGC in the NWTPH-Dx method. Will the findings from the NWTPH-Dx Guidance (Ecology 2022a) project be incorporated into the Draft SGC Guidance (Ecology 2022b) and vice versa?

Response: See prior response to Comment 6.

- (PLIA) Because the use of silica gel is an integral part of the EPH method, absorption of polar organics that are part of the product, or a by-product of degradation, cannot be avoided. In this case and others where silica gel cleanup has been used, the laboratory should use standards that have undergone the same cleanup/separation technique to calibrate the gas chromatograph.

Response: Comment noted. The NWTPH-Dx method study is anticipated to be completed in early 2024 (see Section 4.0) and you will have opportunity to provide comment.

10. (Ryan Hultgren) Sect 1, Paragraph 3. Text: *The extraction method quantifies carbon and hydrogen but doesn't separately quantify the hydrocarbons and the polar metabolites in a sample.*

Comment: The TPH extraction method quantifies extractable organics, including nonpolar hydrocarbons and polar non-hydrocarbons (polar organics). The extracted organics may contain carbon, hydrogen, and oxygen (not just carbon and hydrocarbon) and the polar organics may be derived from multiple sources – biodegradation of petroleum hydrocarbons, components of natural organic matter, or other anthropogenic sources. Suggested change to sentence: “The extraction method quantifies the extractable organics but does not separately quantify the nonpolar hydrocarbons and the polar non-hydrocarbons (polar organics) in a sample.”

Response: We revised the text as: *The extraction and quantitation methods included in Ecology's NWTPH-Dx analysis are not specific to petroleum hydrocarbons, and what is measured includes both non-polar hydrocarbons and non-hydrocarbon polar organics...*

11. (Manchester Lab) Sect 4, first bullet. Text: Do not use SGC without a duplicate sample that is analyzed without SGC.

Comment: SGC and non-SGC analysis can be done on the same sample as long as there is enough sample extract to split between the non-SGC and SGC or if non-SGC analysis is done before the cleanup.

Response: Comment noted. We have included the following text: *For each individual groundwater sample you collect, instruct the lab to split the sample and perform the NWTPH-Dx analysis with and without SGC. Subtract the with SGC NWTPH-Dx result from the no SGC NWTPH-Dx result. Do this for each individual paired result. The difference between the two results (no SGC minus with SGC) is the polar organic concentration.*

12. (Ryan Hultgren) (Sect 5, Paragraphs 1 and 2. Text: This Silica Gel Cleanup guidance supersedes any previous direction from the Department of Ecology including Guidance for the Remediation of Petroleum Contaminated Sites (2012/2016). This guidance should be used in conjunction with Ecology's Analytical Method for Petroleum Hydrocarbons, NWTPH-Dx, with an important update. The NWTPH-Dx directs the user to perform the analysis using SGC and sulfuric acid if the water sample contains biological material. Ecology no longer recommends using concentrated sulfuric acid for analysis with SGC, as it may result in an unintended loss of petroleum products in the sample.

Comment: Please provide more information on why concentrated sulfuric acid is no longer recommended for SGC preparation. Will this be addressed in the guidance resulting from Ecology's Quality Assurance Project Plan Guidance for the WDOE NWTPH-Dx Method for Testing Groundwater, Ecology Publication No. 22-03-101 dated January 2022?

Response: Our analysis found that including sulfuric acid may result in an unintended loss of petroleum hydrocarbon products in the sample, affecting the accuracy of the analysis of the sample.

Additional information will be provided in the update to the NWTPH-Dx method which is expected in early 2024.

13. (Ryan Hultgren) Sect 3, Paragraph 1. Text: The difference in the analytical results provides a measure of the diesel fuel biodegradation components, or polar metabolites.

Comment: The polar metabolites removed by SGC and quantified as DRO may result from biodegradation of gasoline-, diesel-, and oil-range organics, not just diesel-range organics. (Refer to second paragraph of the Results section in Zemo et al. (2017) for discussion of GRO metabolites). Suggested revision: “In the absence of non-petroleum sources of polar organics in groundwater, the difference in the analytical results provides a measure of the petroleum hydrocarbon biodegradation components, or polar metabolites, quantified as DRO.”

Response: That sentence has been removed. We have added the following information:

There are several potential sources of polar organic compounds in weathered petroleum mixtures. In addition to the polar metabolites discussed above, there can be organic compounds from naturally occurring organic matter (such as peat, leaf litter, bark, humic acids), also called biogenic interference (Ecology, 2016; Lundegard, et. al., 2004; ITRC, 2018). There may also be polar organic compounds contained in crude oils (e.g., compounds with nitrogen, sulfur, or oxygen) or other non-petroleum related organic chemicals such as pesticides and phthalates (Mohler et. al., 2013; SF-RWQCB, 2016).

To address potential interference from non-hydrocarbon polar organics with the quantification of petroleum hydrocarbons in soil and groundwater, the NWTPH-Dx method includes a sample cleanup method (i.e., SGC) to remove polar organics (Ecology, 1997). Using SGC in the sample extraction process removes the non-hydrocarbon polar organics and what is measured in the cleaned-up extract are the petroleum hydrocarbons.

Application of Silica Gel Cleanup to Site Media

14. (Ryan Hultgren) The draft SGC Guidance only addresses the use of SGC for groundwater samples. Is it still acceptable to use SGC for soil samples, as stated in Ecology (2016)?

Response: We have added the following information on soil: *Because most soils contain naturally occurring organic matter, use of SGC for soil extracts being analyzed using the NWTPH-Dx method is acceptable, and the results may be compared to our Method A TPH soil cleanup levels.*

Application of Silica Gel Cleanup to TPH Products (e.g., Diesel and/or Oil)

15. (Hooten – Port of Tacoma) The scope of the draft guidance should not be limited to diesel range organics (DRO). It is well established that biological oxidation in groundwater occurs with any release of virtually all petroleum products, including gasoline range organics (GRO), and oil range organics (ORO). The guidance should not discourage the use of silica gel cleanup in groundwater samples obtained at GRO or ORO sites as these data provides useful information regarding the occurrence of biodegradation and help guide the selection of an appropriate remedy.

Response: We added the following text: *You may use SGC as part of the NWTPH-Dx method when analyzing samples collected from sites with diesel and heavy oil range releases to soil or*

groundwater. SGC CANNOT be performed as part of the NWTPH-Gx method to quantify GRO because the cleanup step could result in loss of volatiles. However, the NWTPH-Dx method with SGC could be used to evaluate the contribution from polar organics at sites where GRO was originally released, but the degradation process has proceeded to the point where GRO is no longer detected.

16. (PLIA) Why is ECY indicating not to use SGC on groundwater with both TPH-d and TPH-O?

Response: This language has been removed. See response to Comment 15.

17. (PLIA) Often, when TPH-d breaks down it resembles the heavy oil range and can cause that number to raise on subsequent analysis. Also considering that the guidance for remediation of petroleum contaminated sites deems it inappropriate to split TPH-d and TPH-o when comparing to the CUL, why preclude SGC on GW with both TPH-d and TPH-O?

Response: See response to Comment 15 for use of SGC. We also added the following text: *The NWTPH-Dx method covers the quantitative analysis of semivolatile petroleum products including diesel fuels and heavy oils, and results in a single TPH value that can be used for comparison to Method A cleanup levels (Ecology, 1997). However, if DRO and ORO are reported separately by the laboratory, the results should be summed for comparison with Method A cleanup levels.*

18. (Ryan Hultgren) Please expand on why SGC should not be used when gasoline range organics (GRO) or oil range organics (ORO) are present. In the conceptual model for a weathered DRO plume in Zemo et al. (2017) (used as Figure 1 in this draft SGC Guidance), the “Dissolved Hydrocarbons (HC) Present” refers to the presence of GRO in the sample, with GRO being used as a proxy for a dissolved hydrocarbon plume. Ecology has previously approved use of SGC preparation at a site with DRO and ORO impacts (<https://apps.ecology.wa.gov/cleanupsearch/document/77763>).

Response: This language has been removed. See response to Comment 15 for use of SGC.

19. (Ryan Hultgren) Analytical laboratories often report NWTPH-Dx as DRO and ORO to match MTCA Method A cleanup levels (CULs) in Table 720-1 (for groundwater) for the individual ranges. Ecology (2016) recommends summing the fractionated results (e.g., DRO + ORO) when comparing to the Method A CULs. What carbon ranges does Ecology include when it refers to “DRO” in the draft SGC Guidance?

Response: See response to Comment 17.

20. (Anonymous) Section 4.0 states “Do not use SGC when other ranges of petroleum hydrocarbons, such as gasoline range organics or oil range organics, are present in the groundwater.” This statement effectively limits the use of silica gel cleanup to simple hydrocarbon sites where diesel is the only petroleum contaminant present in groundwater. No supporting documentation is provided for this exclusionary language and justification needs to be provided for this statement. Additionally, the applicability of silica gel cleanup at more complex sites, where multiple hydrocarbon sources may be present, should be determined on a case-by-case basis, based upon site specific data, at the discretion of Ecology and the assigned site manager.

Response: This language has been removed. See response to Comment 15.

21. (Audrey Hackett) In section 4.0, the draft guidance states "Do not use SGC when other ranges of petroleum hydrocarbons, such as gasoline range organics or oil range organics, are present in the groundwater." There are other references to gasoline-range hydrocarbons (GRO) throughout the guidance (including the flow chart and figure in Appendix A and B, respectively), and it is not clear why the presence of GRO at a site or sampling location would preclude the use of silica gel cleanup. Can Ecology clarify in the guidance on why the presence of GRO at a site or sampling location has an effect in the decision-making to use silica gel cleanup?

Response: This language has been removed. See response to Comment 15.

22. (Landau Associates) The draft guidance indicates: "Do not use SGC when other ranges of petroleum hydrocarbons, such as gasoline range organics or oil range organics, are present in groundwater."

- a. The guidance document provides no basis for providing this restriction. We do not believe there should be a restriction for use of SGC where gasoline-range organics (GRO) or oil-range organics (ORO) are present for the reasons indicated below.
 - i. As noted by Zemo et al. 2017, a site where the release was strictly GRO may still create polar metabolites through biodegradation that registers as DRO though no diesel-range organics are present. Conceivably, Northwest diesel-range total petroleum hydrocarbon extended (NWTPH-Dx; without SGC) data for such a site could indicate the presence of DRO that is higher than 500 micrograms per liter (ug/L) and would benefit from the SGC evaluation. Similarly, in our experience, polar metabolites may be detected periodically as ORO at sites with no ORO release; therefore, sites with ORO detections should not be excluded from the SGC evaluation described in this guidance.
 - ii. The NWTPH-Dx method provides quantification of both DRO and ORO. Even when a groundwater plume is known to be solely from a diesel release, ORO are almost always identified by the analysis. This is because diesel fuel typically contains heavier-end petroleum fractions that cross into the oil range. Similarly, when Northwest gasoline-range total petroleum hydrocarbon extended (NWTPH-Gx) analysis is run concurrently, GRO are also almost always identified; again, because the lighter-end fraction of diesel fuel also typically cross into the gasoline range. This prohibition of using SGC if GRO or ORO are present is not reasonable and would eliminate nearly all petroleum sites from being able to use SGC.
 - iii. Many industrial sites have comingled diesel, oil, and/or gasoline plumes. Older sites with these comingled contaminants often have demonstrably high polar metabolite concentrations, or data that indicate a much larger DRO plume than is actually present due to the high proportion of polar metabolites downgradient of the source. So again, this prohibition of using SGC if GRO or ORO is not reasonable would result in businesses having to unnecessarily pay higher remediation costs and long-term monitoring costs.

Response: This language has been removed. See response to Comment 15.

Human Health Toxicity – Polar Metabolites

23. (Grant Hainsworth) I am very appreciative that Ecology is developing guidance regarding this issue. I am certain that you will be receiving comments regarding the toxicity of polar metabolites and recommendations for polar metabolite screening levels that are higher than 500 ug/L. I just wanted to express my support for those comments.

Response: Comment noted.

24. (Hooten – Port of Tacoma) Even if Ecology was authorized to regulate polar metabolites through guidance, the recommended screening level is too low. The 500 ug/L interim screening level in groundwater for the protection of human health is inconsistent with the conceptual model in the cited literature (Zemo, et al., 2017). The screening level is based on a combination of “Stage 1” and “Stage 2” metabolite composition/toxicity ranges. “Stage 1” is the area where dissolved hydrocarbons are present as evidenced by NWTPH-DX laboratory results. “Stage 2” contains no dissolved petroleum and consists entirely of metabolites, as do “Stage 3” and “Stage 4”. A higher weighted average reference dose (RfD) – excluding petroleum metabolites from “Stage 1” plumes – is more applicable to petroleum metabolites in groundwater where petroleum constituents do not exceed MTCA Table 720-1 criteria. This would provide better risk management tool to focus scarce resources at problem sites and eliminate unwarranted work at other low-risk sites.

Response: Our goal was to develop one screening level for polar metabolites that could be conservatively applied to any of the petroleum biodegradation stages, not multiple screening levels or separate ones for each stage. Ecology is not requiring that the composition of polar metabolites be sampled and characterized as part of a site investigation as was done in Zemo (2017). Therefore, there are uncertainties with respect to the specific composition of the polar families at any weathered petroleum site, and we feel that 500 µg/L, for sites with detections of petroleum hydrocarbons in groundwater, is a conservative level even with the uncertainties. There are also uncertainties as to the composition of representative polar compounds within each polar class, and that is why the low end of the toxicity range has been applied at this time.

To better account for the conceptual model in Zemo, 2017, we have developed polar metabolite cleanup levels under two scenarios: for sites that have detectable petroleum hydrocarbons in groundwater, and for sites that do not.

- **Sites with detectable petroleum concentrations in groundwater:** A polar metabolite cleanup level of 500 µg/L is applicable at sites that have detectable concentrations of petroleum hydrocarbons. This cleanup level applies throughout the entire site for compliance purposes, regardless of biodegradation stage.
- **Sites with no detectable petroleum concentrations in groundwater:** A polar metabolite cleanup level of 700 µg/L is applicable at sites that have no detectable concentrations of petroleum hydrocarbons at a PQL of 250 µg/L. This cleanup level applies throughout the entire site for compliance purposes, regardless of biodegradation stage (i.e., Stages 2 through 4). **Note:** Stage 1, which is identified by the presence of dissolved petroleum, cannot be present to use the 700 µg/L polar metabolite cleanup level.

We indicate in the guidance that the drinking water cleanup level and approach for screening polar metabolites may be updated in the future as new toxicity information becomes available including any new information on the composition of polar organics in weathered petroleum.

25. (Dawn Zemo) Thank you for the opportunity to comment on the Washington State Department of Ecology's TCP (Ecology) draft SGC guidance. I applaud Ecology's efforts to take a science-based approach to the issue of the toxicity of petroleum biodegradation metabolites in groundwater that are quantified as "TPH/DRO" unless a SGC is used to separate the hydrocarbons from the (polar) metabolites prior to analysis. I am commenting as an individual who is an expert in this area (publishing since the mid-1990s), and as the senior author of the peer-reviewed publication describing the metabolites plume conceptual model, which is cited to in the draft guidance (Zemo et al 2017) as well as numerous other publications. Also, I have collaborated informally with, and presented seminars/webinars to, Ecology staff at Headquarters and Regional offices on this issue since about 2012.

My comments are focused on the development of the weighted-average toxicity factor and screening level for the metabolites. Specifically, the biggest problem is that by using compositions/toxicity ranges for the combination of "Stage 1" and "Stage 2" as the conservative default for screening purposes, (a) Ecology is not adhering to the conceptual model of the plume, and thus (b) most sites will be "screened in" using a concentration of 500 ug/L. Regarding the conceptual model, the Stage 1 metabolites plume is the condition where dissolved hydrocarbons (HCs) are still detected in the plume (only), which would always be known based on monitoring data, and therefore Stage 1 toxicity should not be used for plumes in which dissolved HCs are not detected (e.g., Stages 2, 3 and 4). Using the conservative toxicity factors for the toxicity/RfD ranges, the metabolites in Stage 1 are 3.5 times more toxic than in Stage 4, so this is a critically important distinction. The Stage 2 metabolites plume is the condition where dissolved HCs are not detected, and the receptor is located within the source area smear zone (only); Zemo et al (2017) states this is not plausible for chronic exposure due to limited groundwater volume in the smear zone. The Stage 4 metabolites plume is the condition where dissolved HCs are not detected, and the receptor is downgradient of the source area smear zone, and is the most plausible for chronic exposure. "Stage 3" was provided in Zemo et al (2017) as combination of Stage 2 (data from source area smear zone) and Stage 4 (data from downgradient of smear zone) data, for use in the unlikely case that the location of smear zone is not known at the site. Regarding the 500 ug/L value, Zemo et al (2017) shows that the average concentration for Stage 4 plumes from more than 20 sites was 730 ug/L. Thus, the 500 ug/L value derived by using Stages 1 and 2 will "screen in" the average highly biodegraded/most plausible condition site and will not be very useful as a risk-management tool.

The conceptual model needs to be adhered to, and therefore the screening level for metabolites should be 2-pronged: (1) plumes with currently detectable dissolved HCs versus (2) plumes without currently detectable dissolved HCs. Regarding potential exposure to the groundwater from within the source area smear zone (Stage 2 conditions), the volume is too small to support chronic exposure. Further, and importantly, Washington State well installation requirements [WAC 173-160-Section 171(b)(v)] state that no drinking water well can be constructed within 100 feet of a "source of contamination" (includes petroleum storage areas and pipelines), which precludes putting the well into the source area smear zone or being within 100 feet of the smear zone. Thus, Stage 2 is implausible, and Stage 4 should be used as the default for plumes without detectable dissolved HCs.

If using only the most toxic end of the toxicity-ranking ranges: the metabolites weighted-average RfD would be about 0.02 mg/kg/d and the screening level would be about 300 to 400 ug/L for plumes in which dissolved HCs are detected (Stage 1); and the metabolites weighted-average RfD would be about 0.07 mg/kg/d and the screening level would be about 1200 to 1400 ug/L for plumes in which dissolved HCs are not detected (Stage 4), rather than 500 ug/L. Recall that the concentration for the average Stage 4 plume from more than 20 sites was 730 ug/L (Zemo et al 2017). Thus, the screening level of about 1200 to 1400 ug/L would be very useful for risk-management purposes.

If due to Washington-specific requirements (e.g., something within MTCA) the WAC regulation for well placement requirements cannot be used to eliminate the potential for contribution from the source area smear zone when developing screening levels, then “Stage 3” could be used as a conservative default. Using the most toxic end of the toxicity-ranking ranges, this would result in a weighted-average RfD of about 0.05 mg/kg/d, and a screening level of about 800 to 1000 ug/L.

At a minimum, the guidance should be revised as described above.

In addition, for your review and consideration, the attached/uploaded White Paper (Zemo, July 2022) provides multiple approaches (with backup) to assigning weighted-average RfDs to the four Stages of the metabolites plumes that do not all default to using the most toxic end of each toxicity-ranking range. They also ultimately make use of the detailed molecular structural class information from Zemo et al Table 1 (2017), in which two classes were by far the most Identified and about which we have abundant toxicity factor information (at least 5 RfDs) (n- and alkyl-acids/esters, and n- and alkyl- alcohols), while still using the toxicity-ranking-range concept. A recommendation is provided in the White Paper: a 2-part screening level with a weighted-average RfD of about 0.04 mg/kg/d and screening level of about 800 ug/L for plumes in which dissolved HCs are still detected, and a weighted-average RfD of about 0.19 mg/kg/d and screening level of about 3800 ug/L for plumes in which dissolved HCs are not detected. Ecology staff would calculate slightly different values for the two screening levels using the MTCA equation.

Please contact me if you have questions about my comments. If the White Paper did not upload properly, please let me know and I will send it by email.

Response: See our response to Comment 24.

Regarding the comment on the smear zone and that no drinking water well can be constructed within 100 feet of a “source of contamination”: Groundwater cleanup levels under MTCA are based on the highest beneficial use and the RME expected to occur under both current and potential future site use. Groundwater is considered potable under MTCA unless all three of the following can be demonstrated (*see* WAC 173-340-720(2)):

- The groundwater is not currently used as drinking water.
- The groundwater is not a potential future source of drinking water for one of the following reasons:
 - a. Insufficient yield (less than 0.5 gallon per minute)
 - b. Contains naturally occurring constituents that make it impractical to use (e.g., total dissolved solids greater than 10,000 mg/L)

- c. Located at a great depth or location that makes it technically impossible to recover.
- It is unlikely that hazardous substances could be transported from the contaminated aquifer to an aquifer that could be used as drinking water.

Local zoning ordinances, such as setbacks, are not considered.

26. (TRC) The focus of TRC's comments relate to the Department of Ecology's (Ecology's) methodology in calculating the interim polar metabolite screening level (SL) of 500 µg/L, which deviates from Zemo, et al. (2017) study and calculates a SL based on the two most conservative stages of a weathered diesel groundwater plume, Stages 1 and 2, shown below in Section 6 of Ecology's draft guidance.

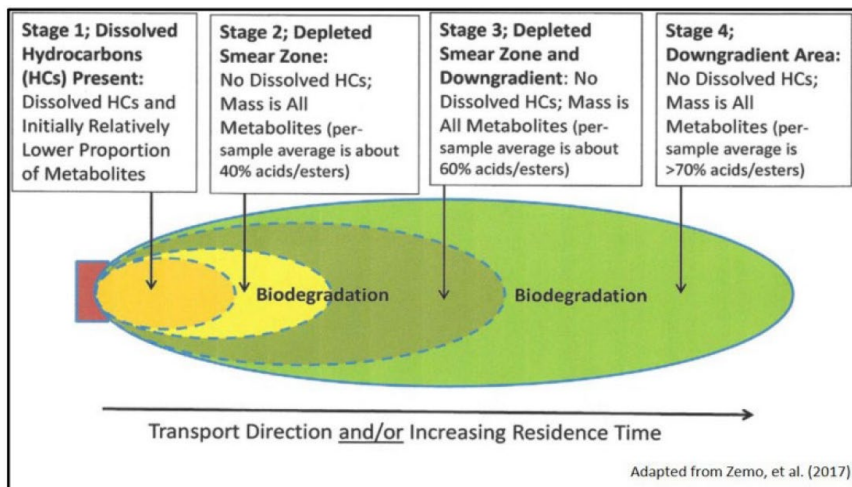
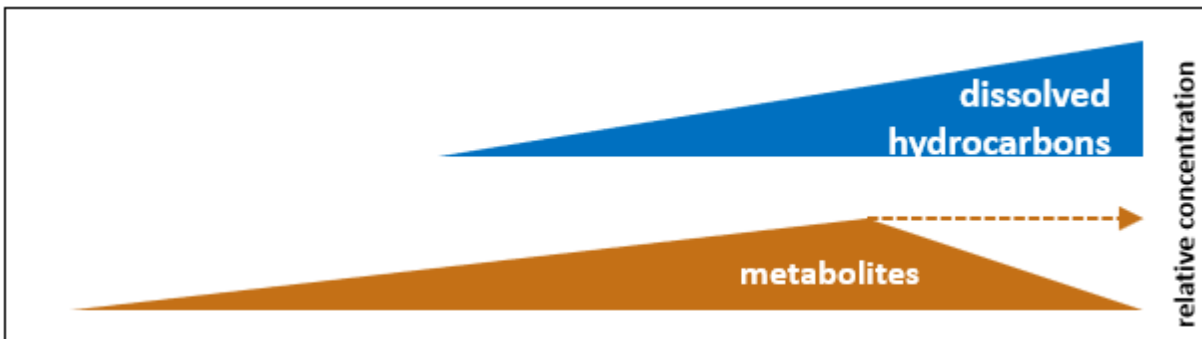


Figure 1: Conceptual model of a weathered groundwater diesel-range organic plume

- a. This scenario uses a weighted average, component fraction approach to calculate a Stage 1 oral reference dose (RfD) of 0.021 mg/kg-d and a Stage 2 oral RfD of 0.037 mg/kg-d. These 2 RfDs are then used to calculate drinking water protective levels for Stage 1 (340 µg/L) and Stage 2 (590 µg/L), which are averaged and rounded up to 500 µg/L to represent the polar metabolite SL protective of all four stages.
- b. In contrast, Zemo et al. (2017) excluded consideration of Stages 1 and 2 and focused on “Stage 3 and Stage 4 metabolites plumes because Stage 1 plumes are defined by GRO and BTEX or other hydrocarbon constituents that would drive risk evaluation and risk management decisions, and Stage 2 plumes have no dissolved hydrocarbons (are nondetect for GRO) but represent the implausible condition of chronically ingesting groundwater only from the smear zone in the source area, which is of limited volume.” If the weighted oral RfDs from Stages 3 and were assumed, the resulting polar metabolite SL would become 1,000 µg/L (using WA Model Toxic Control Act Equation 720-1).
- c. Another interesting figure to consider when looking at polar metabolites is illustrated below showing a release on the right with groundwater flow to the left. In general, concentrations of dissolved hydrocarbons are highest near the source, and diminish as they move downgradient away from the release. On the other hand, since Petroleum Metabolites are a product of biodegradation, their maximum concentrations occur downgradient of the source. Once present in groundwater, metabolites will migrate

further downgradient than dissolved hydrocarbons due to their increased solubility and mobility. This further builds on the Zemo et al. (2017) decision to exclude consideration of Stages 1 and 2, which show limited presence of metabolites in Stage 1.



Natural attenuation of fuels & chlorinated solvents in the subsurface (Wiedemeier et al. 1999)

It's important that Ecology's Draft Guidance for Silica Gel Cleanup in Washington State is based on sound science. Ecology's deviation from the Zemo approach in using only Stage 1 and Stage 2 metabolites is overly conservative for the following reasons:

- Stage 1 plumes are defined by hydrocarbon constituents that would drive the risk values and risk management decisions because the toxicity of hydrocarbon constituents tends to be greater than the toxicity of metabolites. In addition, the Wiedemeier et al. 1999 illustration shows limited presence of metabolites in Stage 1.
- Stage 2 plumes lack hydrocarbon constituents in the dissolved phase and metabolites are primarily located in the shallower LNAPL smear zone, while most drinking water wells are screened at a much deeper interval. In addition, it is highly unlikely that a drinking water source screened near the smear zone would support a typical residential (26 year) exposure duration because of other hydrocarbon-related issues, including aesthetics.

Stage 3 / Stage 4 metabolite plumes are comprised mostly of dissolved phase acids and esters, which will ultimately impact downgradient groundwater supply wells. From an exposure perspective, assuming toxicity values of State 3 / Stage 4 metabolites is appropriate, as Zemo concluded. As mentioned earlier, polar metabolites will migrate further downgradient than dissolved hydrocarbons due to their increased solubility and mobility. Therefore, Ecology's Draft Guidance for Silica Gel Cleanup in Washington State should focus on a Conceptual Site Model (CSM) that incorporates this concept and the risks associated with downgradient receptors, rather than the source area, where metabolites are present in the smear zone and not yet a dissolved-phase concern to deeper drinking water supply wells.

Based on these comments, TRC proposes that Ecology align with Zemo et al. (2017) findings and use Stage 3 and Stage 4 conditions to quantify a polar metabolite SL of 1,000 µg/L (using WA Model Toxic Control Act Equation 720-1).

Response: See our response to Comment 24.

Natural Occurring Organics

27. (Ryan Hultgren) The draft SGC Guidance refers to “polar metabolites” from petroleum hydrocarbon biodegradation frequently but does not mention that polar organics from other sources may be present in groundwater and would also be removed by SGC sample preparation. In the Zemo et al. (2017) research paper referenced in the draft SGC Guidance, the authors acknowledged that polar compounds “can be from natural, nonpetroleum-related sources, or can be from anthropogenic contamination,” but conservatively assumed that identified polar organics in their study were metabolites from the biodegradation of petroleum sources. If this is also Ecology’s assumption, it should be stated.

Note that Ecology guidance and current project documents also refer to potential interference by polar organics characteristic of natural organic matter in groundwater (and soil) including Ecology’s Guidance for Remediation of Petroleum Contaminated Sites, Ecology Publication No. 10-09-057, REVISED June 2016 (Petroleum Remediation Guidance) (Ecology 2016) and Ecology’s Quality Assurance Project Plan Guidance for the WDOE NWTPH-Dx Method for Testing Groundwater, Ecology Publication No. 22-03-101 (NWTPH-Dx Guidance) dated January 2022 (Ecology 2022a).

In Ecology (2016³¹):

“To minimize the potential for interferences by naturally occurring non-petroleum organic matter (such as leaf litter, bark, and peat), the NWTPH-Dx method provides for a silica gel cleanup procedure for removing these naturally occurring organics during the extraction process. Silica gel works by attaching to and removing polar organics, which are characteristic of natural organic matter.”

And:

However, most groundwater does not contain significant levels of naturally occurring organic matter. For this reason, silica gel cleanup should not be used for NWTPH-Dx analyses of groundwater samples unless uncontaminated background samples indicate that naturally occurring organic matter is a significant component of the TPH being detected in the groundwater samples.

In Ecology (2022a³²):

Under guidance by Ecology’s Toxic Cleanup Program, a silica gel cleanup (SGC) step can be employed where groundwater may contain a component of naturally occurring organics that may interfere with the NWTPH-Dx analysis. Since the original publication of the NWTPH method for water, there have been no updates or guidance offered that address possible clarification and improvements to the SGC step.

³¹ Ecology, 2016. *Guidance for Remediation of Petroleum Contaminated Sites*. Publication No. ECY 10-09-057 (June 2016).

³² Ecology’s Quality Assurance Project Plan Guidance for the WDOE NWTPH-Dx Method for Testing Groundwater, Ecology Publication No. 22-03-101 (NWTPH-Dx Guidance) dated January 2022.

Comments/Questions

- Please revise the draft SGC Guidance to include discussion of the presence of non-petroleum related polar organics in groundwater (e.g., from natural organic matter or anthropogenic sources).
- Please provide guidance on determining what constitutes a significant amount of natural organic matter (e.g., a measurement of total organic carbon (TOC) above a certain concentration, chromatographic evidence, etc.) to support using SGC sample preparation with NWTPH-Dx. Ecology has previously (<https://apps.ecology.wa.gov/cleanupsearch/document/77763>) approved use of SGC preparation for groundwater samples based on elevated concentrations of TOC in a background monitoring well at a site with diesel- and oil-range organics (DRO and ORO) impacted groundwater.

Response: We added the following text: In addition to the polar metabolites discussed above, there can be organic compounds from naturally occurring organic matter (such as peat, leaf litter, bark, humic acids), also called biogenic interference (Ecology, 2016; Lundegard, et. al., 2004; ITRC, 2018). Use of SGC can help to reduce or eliminate biogenic interferences from non-petroleum organics that may be in the sample (Ecology, 2016; Ecology 1997). The guidance now discusses options for determining if naturally occurring organics are a significant component of the TPH being detected in the groundwater samples (*see* Section 3.2.1).

28. (Ryan Hultgren) (Sect 5, Paragraph 1). Text: *This Silica Gel Cleanup guidance supersedes any previous direction from the Department of Ecology including Guidance for the Remediation of Petroleum Contaminated Sites (2012/2016).*

Comment: Please address potential for interferences by naturally occurring non-petroleum organic matter in the NWTPH-Dx method for groundwater (and soil) in the SGC Guidance. Ecology's Guidance for Remediation of Petroleum Contaminated Sites, Ecology Publication No. 10-09-057, REVISED June 2016, does not provide direction on how to demonstrate whether polar organics from natural organic matter sources are interfering with NWTPH-Dx results.

Response: See our response to Comment 27.

29. (Grant Hainsworth) My specific comment on the draft guidance is that it focuses entirely on petroleum and polar metabolites but does not address the other interferences that occur with the NWTPH-Dx analysis; primarily when SGC is not used. I think it would be useful to touch on these other interferences and address how they can be incorporated into this process. As an example, it would seem relevant that a background NWTPH-Dx without SGC could be established that would be deducted from the polar metabolites concentration for site where this may be relevant (wood debris, presence of peat, sea water interference, etc.).

Response: See our response to Comment 27.

30. (PLIA) Sect 3, Paragraph 1. Text: Silica gel cleanup (SGC) can be used when testing diesel range organics (DRO) in groundwater when there is evidence of organic materials being present.

Comment: It must be adequately demonstrated that biogenic organic compounds are present in the specific Site's groundwater. This demonstration must be done using multiple lines of

evidence, as indicated below. The following analyses must be performed at each permanent monitoring well location (direct-push installed temporary wells and reconnaissance/grab groundwater samples are not acceptable) where SGC is intended to be used:

- a. Quantification of TOC using EPA Method 5310 or approved alternative.
- b. Groundwater samples should be “split” by the laboratory and performance of NWTPH-Dx analyses with and without SGC performed.
- c. Chromatograms are reviewed for specific chemical signatures indicating the presence of organic compounds (reviewed by a chemist with experience in chromatographic interpretation).
- d. Laboratory chromatograms for each sample must be included with the data package. All analytical reports must clearly stipulate whether SGC was used in the sample preparation process.
- e. Provide quantification of TOC using EPA Method 5310 or approved alternative method at a background location that is representative of the site and approved by PLIA. (Note: The background location cannot display evidence of petroleum impacts (as documented through analytical data). Prior approval of the background location is required by the Agency.

Response: See our response to Comment 27. We also added the following: Characterizing the contribution from naturally occurring organics in groundwater to the TPH totals may be done by analyzing clean representative background samples (upgradient of the source) from permanent monitoring wells. Temporary well points and grab groundwater samples may not be used to establish whether naturally occurring organics are present in groundwater. Background data should account for seasonal variation and should not contain any measurable petroleum hydrocarbons. In addition, background data should include quantification of total organic carbon (TOC) using Environmental Protection Agency (EPA) Method 5310 or an approved alternative, and a review of chromatograms for signatures indicating the potential presence of polar organics. Polar organic concentrations identified within and downgradient of the plume may be adjusted if the contribution from naturally occurring organics (if any) is determined from representative background wells.

Site Investigation and Compliance

31. (PLIA) The SGC analyses should be performed only on groundwater from a permanent monitoring well location (direct-push installed temporary wells and reconnaissance/grab groundwater samples are not acceptable).

Response: We added the following text: When using SGC, you should analyze groundwater samples from permanent monitoring wells both with and without applying SGC.

32. (Suzanne Dolberg) The guidance specifies a method for calculating the 95% UCL; but the method may not be appropriate because the Ecology method implicitly assumes that the data are normally distributed, which is not normally the case at most sites. The guidance should allow for the use of software such as USEPA's ProUCL for calculating the UCL.

Response: The methodology for calculating the 95% UCL has been removed. Please follow our MTCA Rule language regarding compliance monitoring requirements for groundwater. [173-340-720 \(9\)](#). Also see our 1992 [Ecology Statistical Guidance for Ecology Site Managers](#)³³.

33. (Suzanne Dolberg) The guidance is not clear on whether the 95% UCL should be calculated for the whole site or individual wells and which of those values are considered for compliance determinations.

Response: In accordance with our MTCA Rule, compliance with groundwater cleanup levels shall be determined for each groundwater monitoring well. [173-340-720 \(9\)\(c\)\(iv\)](#).

34. (Ryan Hultgren) Sect 3, Blue Text Box. Text: You can use the difference in the analytical results from the different sampling locations and collection times to evaluate the attenuation of DRO and develop a quarterly groundwater monitoring frequency.

Comment: Not all sites will require a quarterly monitoring. For example, long-term compliance monitoring may include semiannual, annual, biennial, or less frequent monitoring. Suggested revision to end of sentence: "...develop a groundwater monitoring frequency."

Response: This information has been removed from the guidance. Please follow see our 2016 [Guidance for Remediation of Petroleum Contaminated Sites](#)³⁴ for guidance on compliance monitoring and evaluating natural attenuation.

35. (PLIA) Sect 4, 2nd Bullet. Text: Do not use SGC when other ranges of petroleum hydrocarbons, such as gasoline range organics or oil range organics, are present in the groundwater.

Comment: The following analyses must be performed at each permanent monitoring well location (direct-push installed temporary wells and reconnaissance/grab groundwater samples are not acceptable).

Response: See our response to Comment 31.

³³ <https://apps.ecology.wa.gov/publications/SummaryPages/9254.html>

³⁴ <https://apps.ecology.wa.gov/publications/SummaryPages/1009057.html>

Regulating Polar Metabolites as Hazardous Substances

36. (Scott Hooten – Port of Tacoma) Petroleum is defined as a hazardous substance under MTCA. The draft guidance acknowledges that polar metabolites are not petroleum. Formal rulemaking is required to designate polar metabolites as a MTCA hazardous substance. The recommended screening level for polar metabolites should only be established if formal rulemaking establishes petroleum metabolites as hazardous substances under MTCA. The universe of Hazardous Substances over which Ecology exercises its cleanup authority is defined by statute¹ and the implementing regulation². The Port respectfully requests that Ecology explain why polar metabolites³ can be regulated under MTCA as Hazardous Substances. It is understood that the definition of hazardous substances includes “any substance or category of substances, including solid waste decomposition products, determined by the director by rule [emphasis added] to present a threat to human health or the environment if released into the environment.” Ecology should not attempt expand the universe of hazardous substances subject to MTCA authority through guidance when formal rulemaking is required. The Port has raised this issue in comments to Draft Guidance for Remediation of Petroleum Contaminated Sites in 2011 and 2012 (see attached); however, Ecology did not respond to our prior comments on this issue.

Response: Polar metabolites are degradation by-products of petroleum. Accounting for degradation by-products is a factor that is considered when identifying hazardous substances for the purpose of defining site cleanup requirements ([WAC 173-340-703\(1\), \(2\)\(g\); 173-340-200](#)). Many of the representative substances that make up the polar metabolite families/structural classes are regulated under MTCA and CERCLA or are listed dangerous wastes (i.e., “U” listed wastes). Based on a review of human-health criteria (i.e., RfD) obtained data from regulatory databases such as IRIS and EPA’s PPRTV program, these by-products have shown to be toxic and, in some cases, more toxic than the parent petroleum hydrocarbon.