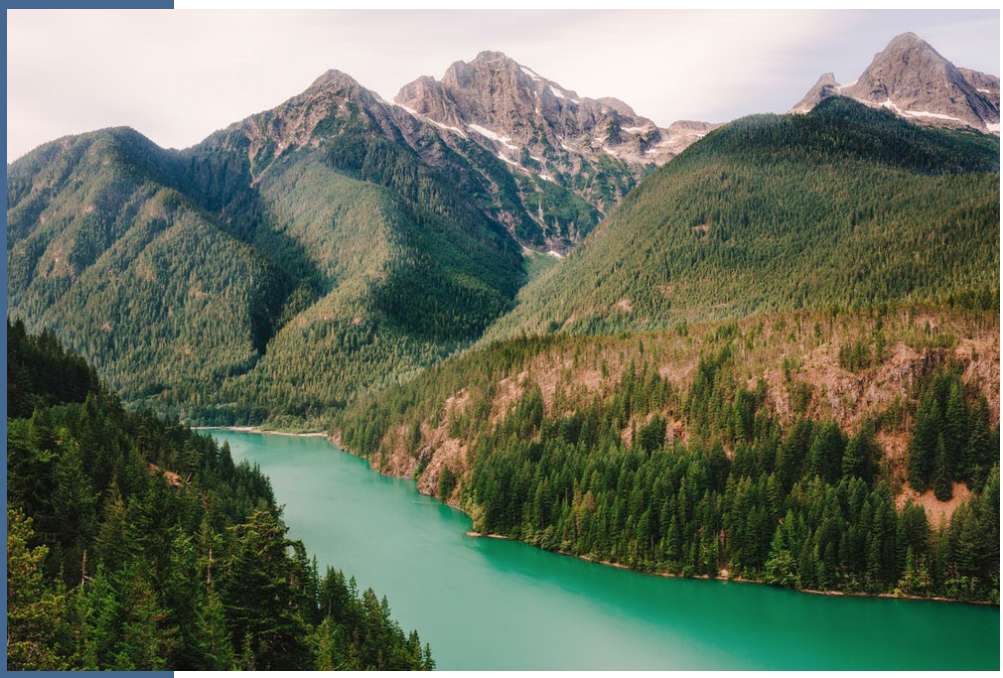

# Draft Guidance for Silica Gel Cleanup in Washington State

Toxics Cleanup Program
Washington State Department of Ecology
Olympia, Washington

September 2022

Publication No. 22-09-059

DEPARTMENT OF ECOLOGY
State of Washington

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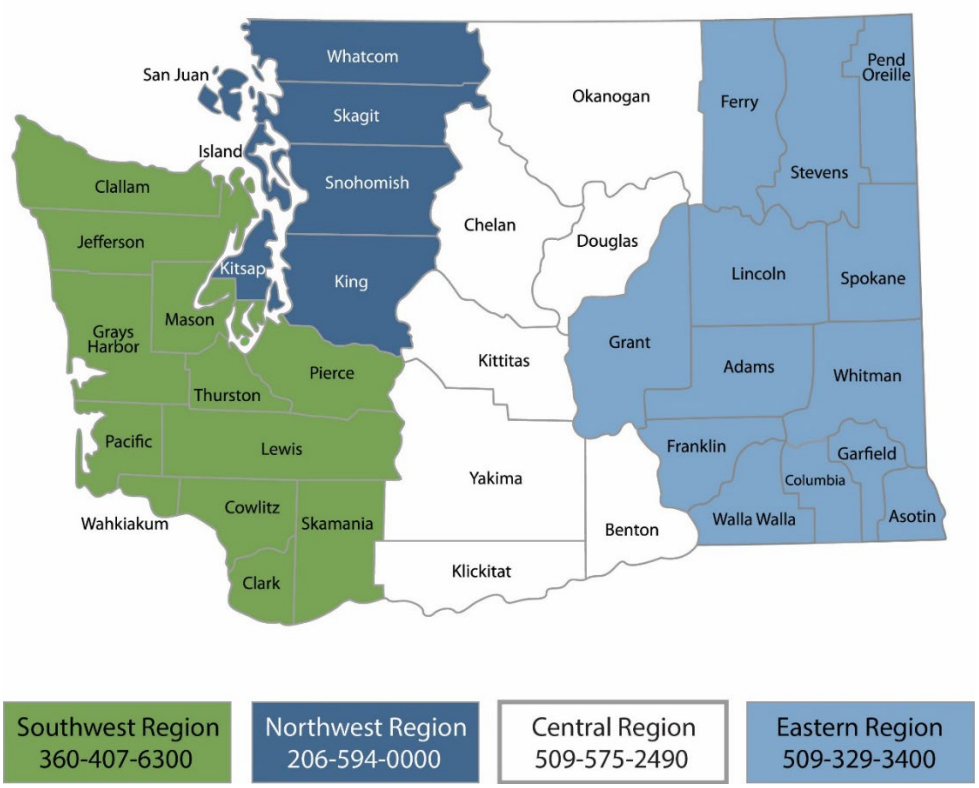


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**Table 1:** Acronyms and abbreviations

| Acronym & Abbreviations | Definition |
|---|---|
| **TPH** | Total petroleum hydrocarbons |
| **DRO** | Diesel range organics |
| **USEPA** | United State Environmental Protection Agency |
| **SGC** | Silica gel cleanup |
| **NWTPH-Dx** | Qualitative and quantitative method 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. |
| **HC** | Hydrocarbons |
| **UCL** | Upper confidence limit |
| **MOE** | Margin of error |
| **ug/L** | Micrograms per litre |

# 1.0 Introduction

Groundwater samples are routinely collected and analyzed for total petroleum hydrocarbons (TPH), which include the gasoline range organics, diesel range organics (DRO), and oil range organics.

Over time, petroleum dissolved in groundwater naturally biodegrades through a microbial oxidative process into hydrocarbons and polar metabolites[2]. Hydrocarbons contain carbon and hydrogen and are non-polar in molecular structure. Polar metabolites have carbon, hydrogen and oxygen and are polar in molecular structure.

Ecology's analytical methods to test for TPH are based on the United States Environmental Protection Agency (USEPA) method 8015D[3]. Prior to quantifying a sample, organics are separated from water by a funnel and liquid-liquid extraction method using a solvent (see EPA Method 3510C)[4]. The extraction method quantifies carbon and hydrogen, but doesn't separately quantify the hydrocarbons and the polar metabolites in a sample.

Because polar metabolites are not petroleum, and do not have the same toxicity as petroleum, TPH analysis may provide results that are biased high under certain conditions. It may also result in monitoring groundwater over timeframes that are longer than necessary.

# 2.0 What is Silica Gel Cleanup?

Silica gel cleanup is a process where silica gel can be used in TPH analysis to adsorb the polar metabolites and remove or greatly reduce non-hydrocarbons from groundwater sample extracts.

# 3.0 When should Silica Gel Cleanup be used?

Silica gel cleanup (SGC) can be used when testing diesel range organics (DRO) in groundwater. When using SGC, you should analyze groundwater samples both with and without applying SGC. The difference in the analytical results provides a measure of the diesel fuel biodegradation components, or polar metabolites.

A screening level will apply for the level of polar metabolites (discussed in section 12.0), as well as either Ecology's current cleanup level for DRO or a site-specific cleanup level. 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.

Appendix A provides a decision matrix for using SGC.

# 4.0 When should SGC not be used?

- Do not use SGC without a duplicate sample that is analyzed without SGC.
- Do not use SGC when other ranges of petroleum hydrocarbons, such as gasoline range organics or oil range organics, are present in the groundwater.

[2] Polar metabolites include ketones, phenols, aldehydes, alcohols, and acids/esters. As samples biodegrade and move away from the sources the proportion of acids/esters as compared to the other polar metabolites tends to increase.
[3] https://www.epa.gov/sites/default/files/2015-12/documents/8015d_r4.pdf
[4] https://www.epa.gov/sites/default/files/2015-12/documents/3510c.pdf

## 5.0 Update to existing guidance

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)[5].

This guidance should be used in conjunction with Ecology's *Analytical Method for Petroleum Hydrocarbons*, *NWTPH-Dx*[6], 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.

## 6.0 The weathered diesel plume in groundwater sampling

In groundwater, the relative proportion of polar metabolites to hydrocarbons (and the percentage of acids/esters within the metabolites fraction) typically increases over both time and distance from the source area. See Figure 1.

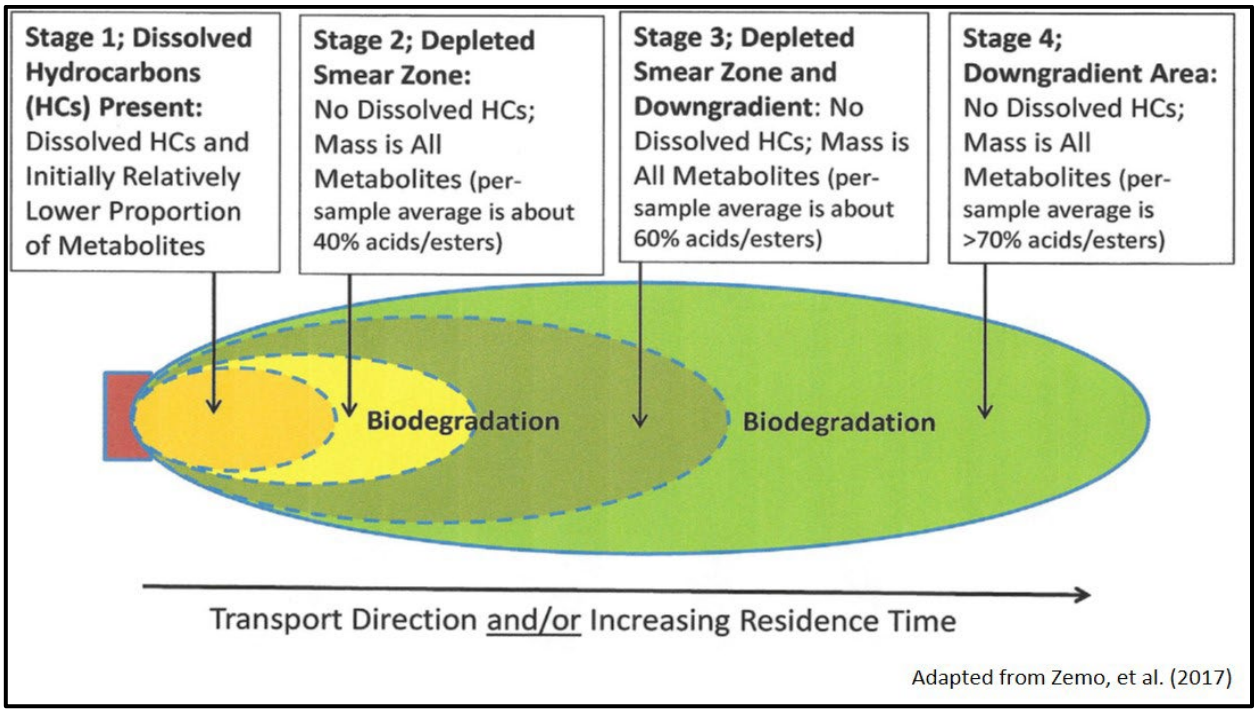


**Figure 1:** Conceptual model of a weathered groundwater diesel-range organic plume

As shown, a typical weathered diesel groundwater plume is comprised of four stages (Zemo, et al., 2017). The area closest to the source is Stage 1, where dissolved hydrocarbons are detected and there is a lower proportion of polar metabolites. Stage 2 is identified by the lack of dissolved hydrocarbons. As samples continue to biodegrade and move into the other stages, the proportion of acids/esters as compared to the other polar metabolites tends to increase. See Appendix C for more information.

[5] https://apps.ecology.wa.gov/publications/documents/1009057.pdf
[6] https://apps.ecology.wa.gov/publications/SummaryPages/97602.html

It is important to know when a DRO contaminated groundwater sample may contain primarily polar metabolites, as the analysis may need to incorporate SGC to distinguish between the hydrocarbons and the polar metabolites.

## 7.0 Collection of samples for analysis and monitoring

Seasonal water table fluctuations may affect groundwater flow and the presence of DRO in the dissolved plume. It is necessary to collect multiple samples over time, and apply SGC to the analysis, to demonstrate whether or not the DRO concentrations are consistently less than the cleanup level. The following approach should be used to determine the number of samples to be collected.

- Using historical time series data collected for the site, calculate a 95% upper confidence limit (UCL). Compare the 95% UCL value with the cleanup level.
    - If the 95% UCL is less than the cleanup level, no further groundwater monitoring is required.
    - If the 95% UCL is greater than the cleanup level, collect samples quarterly for one year and analyze both with and without SGC. Quarterly samples help assess the impact of seasonality on the site data across time.
        - After one year, calculate the 95% UCL data. If the 95% UCL data is less than the cleanup level, no further groundwater monitoring is required.
- If you don't have historical time series data for the site, establish multiple monitoring locations and collect and analyze quarterly samples for at least a year.

As some polar metabolites are more soluble than others, it is important to collect samples from all sampling locations to identify where polar metabolites have migrated and so not to yield a data bias. Additionally, it is recommended to analyze groundwater samples both with and without SGC for all locations, including those where the groundwater DRO concentrations exceed the cleanup level. See Appendix B for an example of the potential effects of applying SGC to sample.

## 8.0 Assessing the analytical results

To assess attenuation of DRO in the groundwater at your site, compare the difference between the results of the samples analyzed with and without SGC.

If the analytical results from all the samples both with and without SGC yield concentrations that are less than the cleanup level, or are nondetects (analytical samples where the concentration is lower than can be detected), no further groundwater monitoring is necessary.

If any analytical sample results using SGC indicate concentrations that are greater than the cleanup level, calculate a 95% UCL of the SGC data.

To do this, first calculate the margin of error (MOE) of the time series data:

$$\text{Equation 1: } \mathrm{MOE} = \mathrm{Z} * \frac{\mathrm{S}}{\sqrt{\mathrm{n}}}$$

Where:

MOE=margin of error

Z = 1.96 (sample size >20* and 95% level of confidence)
S = standard deviation
N = sample size

*If the sample size is <20, use the appropriate Student t value with n-1 degrees of freedom.

To calculate the 95% UCL, calculate the average concentration and add that value to the margin of error:

Equation 2: $95\%\ UCL = \bar{x} + MOE$

Where:

$\bar{x}$ = average concentration

MOE = margin of error

If the 95% UCL result with SGC is less than the cleanup level, no further groundwater monitoring is necessary.

If the 95% UCL result with SGC is greater than the cleanup level, continue quarterly monitoring until the 95% UCL is less than the cleanup level.

## 9.0 Conditional point of compliance

Groundwater cleanup activities must use methods that meet cleanup levels throughout the site. Determining if cleanup levels have been achieved is accomplished through groundwater compliance monitoring. Under certain conditions, Ecology may approve a conditional point of compliance under WAC 173-340-720(8)[7].

You may also request a conditional point of compliance when using SGC and calculating a 95% UCL based on the SGC results. To increase understanding of site conditions at the time of sample collection, use all relevant SGC results to calculate a single 95% UCL. Ecology recommends using a minimum of data from four consecutive quarters from all well sites using SGC and proposing a conditional point of compliance.

## 10.0 Nondetect results

If your DRO sampling yields a high percentage of nondetect results, you may propose the use of alternate methods[8] such as a random value (e.g. Excel random number function) between zero and the detection limit or using ProUCL 5.2 software (USEPA).

## 11.0 Natural attenuation remedy

Contaminated sites where SGC has demonstrated the presence of a weathered groundwater diesel plume may be potential candidates for monitored natural attenuation as a remedy. The dominance of polar metabolites shown by the SGC results is evidence of natural attenuation (intrinsic biodegradation) occurring in site groundwater. If you are considering proposing natural

[7] https://apps.leg.wa.gov/WAC/default.aspx?cite=173-340-720
[8] This guidance is consistent with WA 173-340-720(9) and Statistical Guidance for Ecology Site Managers.

attenuation as a remedy, refer to WAC 173-340-370(7)[9] and the *User's Manual: Natural Attenuation Analysis Tool Package for Petroleum-Contaminated Ground Water*[10].

If monitored natural attenuation remedy is viable for the site, the 95% UCL should be calculated site wide, from all time-series data and at all sampling locations.

# 12.0 Toxicity of polar metabolites

## 12.1 Human health

Ecology is currently reviewing the available information regarding the toxicity of polar metabolites to human health via the drinking water pathway. Until this review is completed, Ecology recommends using the interim screening level for polar metabolites of 500 ug/L to protect human health at DRO-contaminated sites. This screening level is derived from Zemo, et al. (2017) and characterizes the chemical structure and potential toxicity of polar metabolites measured as DRO in groundwater samples taken at biodegrading fuel impacted sites. See Appendix C for more information.

## 12.2 Environment - aquatic

Ecology has recently studied the aquatic toxicity of polar metabolites at weathered diesel plumes (Ecology, 2020) and recommends the following cleanup goals:

- Freshwater species = 3,040 ug/L
- Marine species = 2,120 ug/L

[9] https://app.leg.wa.gov/WAC/default.aspx?cite=173-340-370
[10] https://apps.ecology.wa.gov/publications/documents/0509091a.pdf

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# Appendix A

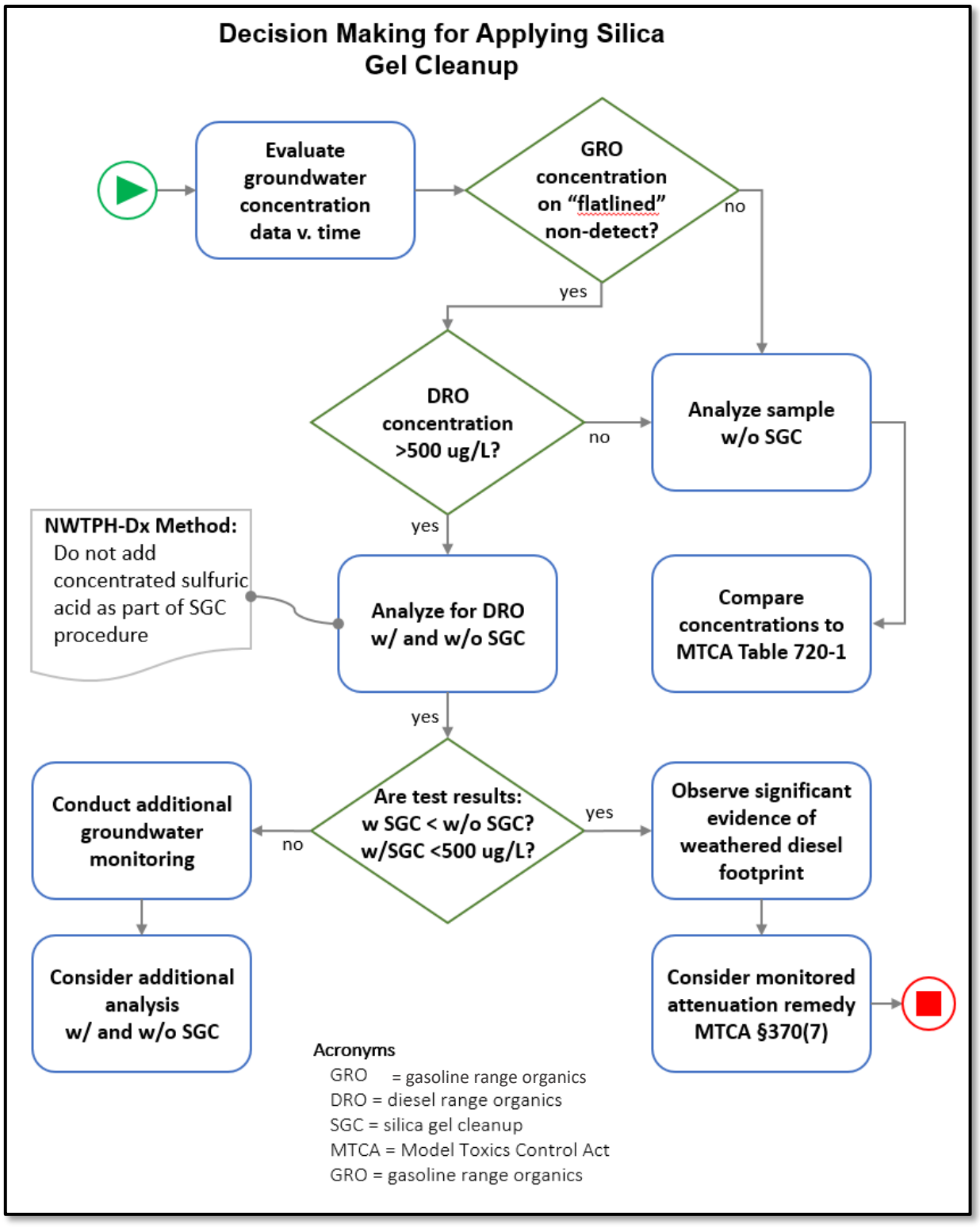


**Figure 2:** Diagram for decision making when applying silica get cleanup

## Appendix B

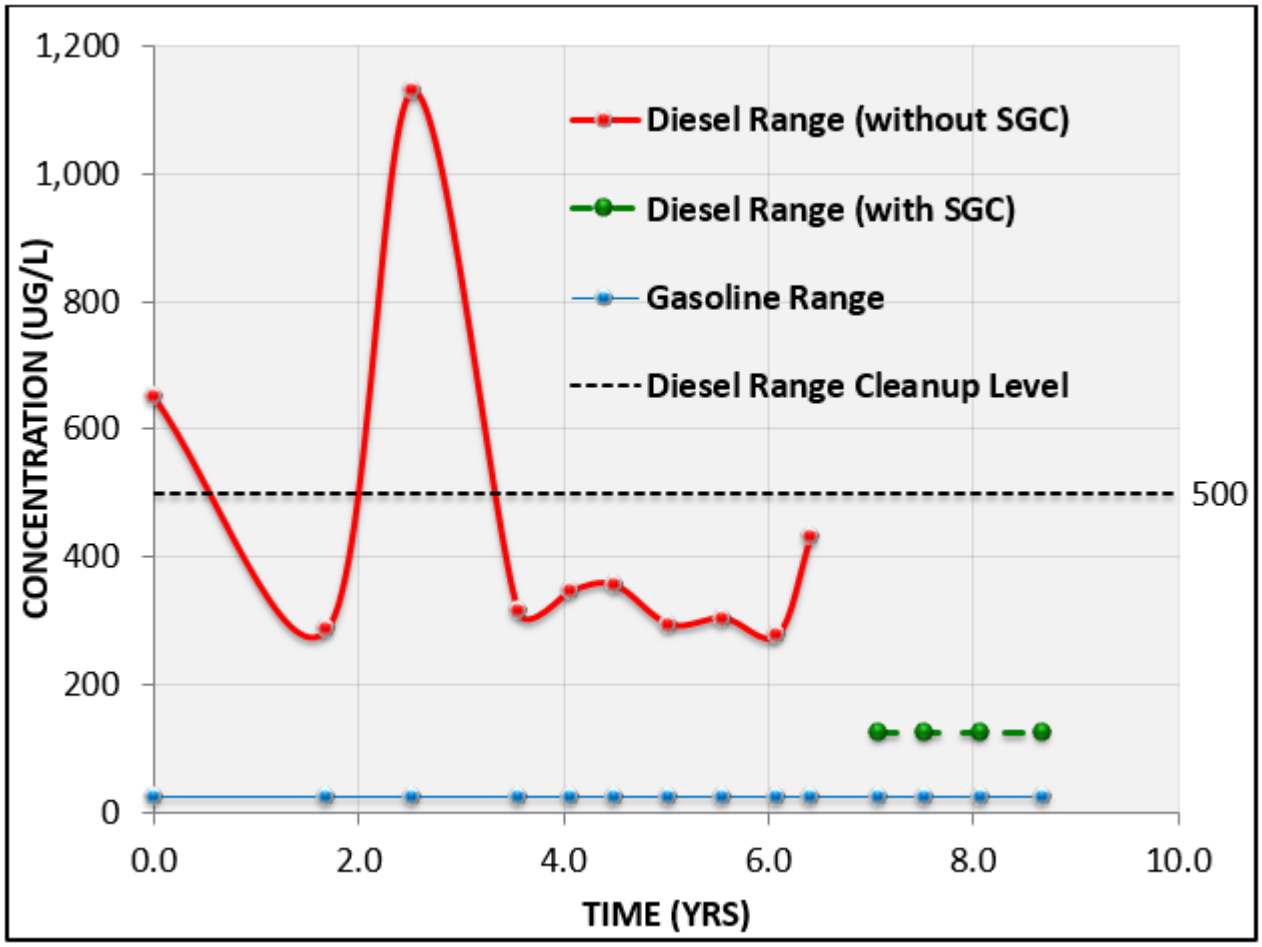


**Figure 3:** Example of concentrations of gasoline-range organics and diesel-range organics both with and without silica gel cleanup at one sampling location over time

# Appendix C: Human Toxicity of Polar Metabolites – Derivation of Screening Level

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

## 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 identifying five families and 22 structural classes of polar metabolites that are expected to result from the aerobic and anaerobic biodegradation of petroleum (see Appendix D).

## 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); and 2) the Texas Commission on Environmental Quality (TCEQ) Protective Concentration Levels (PCLs). Both databases use EPA's Integrated Risk Information System (IRIS) as the preferred source of toxicity data. An expanded toxicity assessment included 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.

The toxicity assessment resulted while identifying 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 individual toxicity rankings included: low (RfD≥0.1 mg/kg/day), low to moderate (RfD≥0.01 to <0.1 mg/kg/day), and moderate (RfD≥0.001 to <0.01 to mg/kg/day). Appendix B lists the toxicity rankings for each of the 22 structural classes.

Ecology compared the toxicity values from 2012 with more recent values from 2021. This included a review of our Cleanup Levels and Risk Calculation (CLARC) database, EPA's fall 2021 RSL table, and TCEQ's January 2021, PCL table. This review resulted in only one potential change in the toxicity ranking applied to a structural class.

Benzophenone is a polycyclic aromatic ketone with a published oral RfD of 0.0067 mg/kg-day (TCEQ 2021 value). 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.

# 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 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 Appendix D and Figure 3). The unique polar metabolites tentatively identified in each sample using the non-targeted full-scan approach were categorized into their respective polar family, structural class, 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 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.

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 3 is 95% low, 5% low to moderate, and 0% moderate.

## Polar Metabolite Screening Level

A conservative approach to developing a polar metabolite screening level is to apply the low end of the toxicity range to the percent composition identified for each polar family/class as identified in Appendix D. The low end of the oral RfD toxicity range is identified as follows: 0.1 represents low toxicity, 0.01 represents low to moderate toxicity, and 0.001 represents moderate toxicity. As an

example using Appendix B data, the Stage 1 metabolite mixture consists of 78% at an oral RfD of 0.1, 20% at 0.01, and 2% at 0.001. With few exceptions, this approach applies the most conservative RfDs (i.e., lowest RfD) resulting from the toxicity assessment for each polar family/class. A few exceptions are noted below. However these compounds were shown to be non-detect in the targeted analysis at a low reporting limit of generally 10 ug/L.

### 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 a toxicity value of 0.1 or higher. Therefore, the class was assigned a 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 a toxicity value of 0.1 or higher. Therefore, the class was assigned a 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 a toxicity value of 0.01 or higher. Therefore, the class was assigned a low to moderate toxicity.

### Ketones (Polycyclic aromatic)

9,10-Anthraquinone 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 a toxicity value of 0.01 or higher. Therefore, the class was assigned a low to moderate toxicity.

### Phenols (non-C14 Alkyl phenols)

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

To be conservative, both Stages 1 and 2 were used to develop a screening level for polar metabolites, since the average toxicity of the metabolite mixture decreases with each progressive stage. To develop the screening level, weighted oral RfDs were derived, based on the total average toxicity of the mixture for the first Stages 1 and 2 using the formulas below along with the data in Appendix B.

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

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

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

The weighted oral RfDs these three questions result in drinking water protective levels (at two significant figures) of 340 ug/L for Stage 1 and 590 ug/L for Stage 2 (using Model Toxic Control Act Equation 720-1). Combining Stage 1 and 2 results yields an average polar metabolite screening level of 470 ug/L. This value is rounded up to 500 ug/L to represent an overall polar metabolite protective level that can be applied to any of Stages 1 through 4.

While Ecology is reviewing information related to human health toxicity of polar metabolites via the human health drinking water pathway, in the interim, use the polar metabolite interim screening level of 500 ug/L to demonstrate human health protectiveness for any of Stages 1 through 4.

## Application of the Polar Metabolite Screening Level

TPH groundwater levels measured using method NWTPH-Dx without SGC may be as high 1,000 ug/L as long as it is shown that both portions of the TPH mixture (i.e., dissolved petroleum and polar metabolites) are both less than 500 ug/L (Table 1).

**Table 2**: Application of the polar metabolite screening level

| TPH Analytical Method | Concentration (ug/L) |
|---|---|
| NWTPH-Dx (no SGC) =<br>Total TPH (dissolved petroleum + polar metabolites) | 1,000<br>(initial screening level) |
| NWTPH-Dx (with SGC) =<br>dissolved petroleum | 500<br>(not to exceed level) |
| [NWTPH-Dx (no SGC)] – [NWTPH-Dx (with SGC)] =<br>polar metabolite concentration | 500<br>(not to exceed level) |

# Appendix D:

**Table 3**: Summary of structural classes of toxicity for biodegradation, stages 1 through 4

| Polar family | Specific structural class | Expected chronic oral toxicity to humans[2] | Biodegradation stages[1] | | | |
|---|---|---|---|---|---|---|
| | | | stage 1 | stage 2 | stage 3 | stage 4 |
| | | | Per-sample average %[3] | | | |
| 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:
1 Stages: 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).
2 The approximate toxicity of each polar subclass is estimated based on toxicity data for individual chemicals within the subclass. The Oral Reference Dose (RfD) is expressed in mg/kg/day as low for RfDs $\geq$ 0.1; low to moderate for RfDs <0.1 to 0.01; and moderate for RfDs <0.01 to 0.001.
3 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.
4 Where identified, 2,4- and 3,5-ditertbutylphenol (DTBP) are classified as alkyl phenols but are assigned a low toxicity ranking based on toxicity data for the di-substituted alkyl phenol category from USEPA (2009).
5 Total Avg. Tox. L/ L-M/ M = averages in percent for each toxicity classification for each Stage; "low"/"low to moderate"/"moderate".
This table is modified from Zemo, et al. (2017).