Guidance for the WDOE NWTPH-Dx Method for Testing Groundwater

Silica Gel Cleanup Protocol Revision

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Contact Information

Publications Team
Environmental Assessment Program
Washington State Department of Ecology
P.O. Box 47600
Olympia, WA 98504-7600
Phone: 360-407-6764

Washington State Department of Ecology — https://ecology.wa.gov
- Headquarters, Olympia   360-407-6000
- Northwest Regional Office, Shoreline   206-594-0000
- Southwest Regional Office, Olympia   360-407-6300
- Central Regional Office, Union Gap   509-575-2490
- Eastern Regional Office, Spokane   509-329-3400

Guidance on the WDOE NWTPH-Dx Method for Testing Groundwater

Silica Gel Cleanup Protocol Revision

by

William Hobbs

Toxic Studies Unit, Environmental Assessment Program
Washington State Department of Ecology
Olympia, Washington

Karin Bailey, Joan Protasio and Christina Frans

Manchester Environmental Laboratory, Environmental Assessment Program
Washington State Department of Ecology
Olympia, Washington

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EAP: Environmental Assessment Program
ERO: Eastern Regional Office
CRO: Central Regional Office
WQP: Water Quality Program

HQ: Headquarters
NWRO: Northwest Regional Office
SWRO: Southwest Regional Office
TCP: Toxics Cleanup Program

Abstract

In 1997, the Washington State Department of Ecology (Ecology) published analytical methods for analyzing total petroleum hydrocarbons (TPH) (NWTPH; Ecology 1997). Under guidance by Ecology's Toxic Cleanup Program (TCP), a silica gel cleanup (SGC) step can be employed where groundwater may contain a component of naturally occurring polar compounds that may interfere with the NWTPH analysis for diesel range organics (DRO). The goal of this project was to provide an updated protocol on how laboratories use silica gel cleanup (SGC) on groundwater samples contaminated with weathered DRO.

Twenty-three regional labs accredited by Ecology for the NWTPH method were surveyed to determine what SGC protocols are being used. Thirteen labs responded, and current protocols varied across labs. Manchester Environmental Laboratory (MEL) wrote and tested a revised SGC protocol based on published silica gel column approaches and EPA Method 3630. The revised protocol also incorporated a reverse surrogate of decanoic acid to evaluate the efficacy of removing polar compounds.

Seven of the 13 contract labs agreed to participate in a paid inter-laboratory comparison study with MEL to evaluate the revised protocol. The results of the inter-lab study showed that the revised SGC protocol is repeatable and reproducible among the labs. TCP should begin disseminating the revised protocol internally to site managers and consider revising the NWTPH method guidance.

Introduction

In 1997, the Washington State Department of Ecology (Ecology) published analytical methods for petroleum hydrocarbons (Ecology 1997). These methods are directly related to compliance with the Model Toxics Control Act (MTCA) Cleanup Regulation (chapter 173-340 WAC). Under Part VII of the MTCA Cleanup Regulation, Method A is one of the most common approaches to establishing cleanup levels for groundwater impacted by hydrocarbons. Under Method A of the regulation, a total petroleum hydrocarbon (TPH) approach may be taken. The process of evaluating TPH includes two methods[1]:

- NWTPH-Gx — gasoline range organics (GRO)
- NWTPH-Dx — diesel range organics (DRO)

The GRO and DRO methods capture light and heavy molecular weight compound ranges, respectively. The DRO method also captures residual heavy oil compounds (e.g., Bunker C), referred to herein as residual range organics (RRO). The DRO method can also capture petroleum degradates or metabolites that are non-hydrocarbon polar compounds.

Under Ecology's Toxic Cleanup Program (TCP) guidance, a silica gel cleanup (SGC) step can be employed where groundwater may contain a component of naturally occurring polar (non-petroleum) organics that may interfere with the NWTPH-Dx analysis. The SGC step is written into the Ecology TPH Methods document (Ecology 1997) and is intended to remove polar (non-petroleum) organic compounds from the sample extract before analysis on the gas chromatograph.

The current guidance on using SGC on groundwater samples for contaminated site investigations and cleanup is that NWTPH-Dx concentrations must be measured with and without SGC to be considered in a site assessment (Ecology 2016). Furthermore, SGC should only be used on groundwater samples if there is a significant component of naturally occurring organics, as established by DRO measurements on groundwater from an on-site background well.

Since the original publication of the NWTPH method for water, no updates or guidance have been offered that address possible clarification and improvements to the SGC step. In particular, the current SGC step calls for silica gel to be added as free-flowing in a "shake" method; however, a silica gel column method based on EPA Method 3630C (EPA 1996), has been shown to have a higher removal efficiency of polar compounds (Zemo et al. 2013). In addition, the SGC step calls for using sulfuric acid before adding silica gel, which can remove some of the heavier sulfur-containing hydrocarbons. This step is not routinely carried out on groundwater samples by Ecology's Manchester Environmental Laboratory (MEL) unless specifically requested. Whether other regional labs routinely use the complete NWTPH-Dx method or a modified version on

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[1] NWTPH: Northwest total petroleum hydrocarbons, where NWTPH-Gx is in the carbon range C7-C12 and NWTPH-Dx is in the carbon range C10-C24.

groundwater samples is unknown. Inconsistencies in how the SGC step is currently being carried out and improved technologies for the SGC step are the main reasons for this study.

The goal of this project was to provide guidance on how laboratories should use silica gel cleanup (SGC) on groundwater samples contaminated with weathered diesel range organics (DRO). To accomplish this, we (1) surveyed accredited labs to ascertain how the NWTPH-Dx method is currently being used, (2) wrote a revised SGC protocol with feedback from regional accredited laboratories based on a combination of Zemo et al. (2013) and EPA 3630C for NWTPH-Dx, and (3) conducted an interlaboratory comparison of the revised protocol on groundwater samples containing weathered DRO.

Methods

Participating Laboratories

There are 31 laboratories in 10 different states accredited by Ecology for the WDOE NWTPH-Dx method in non-potable waters. Within the Pacific Northwest region (Washington, Oregon, and Idaho), there are 23 accredited laboratories (Table 1). Thirteen of the labs provided their internal Standard Operating Procedure (SOP) for the analysis of NWTPH-Dx, including the SGC protocol. Eight labs agreed to receive contract samples and a revised SGC protocol in an interlaboratory comparison; all labs were paid for the analysis. For the remainder of the report, lab results will be anonymous. The original laboratory reports and EDDs will not be included in this report.

Table 1. List of laboratories accredited by Ecology for the WDOE NWTPH-Dx method.

State	City	Laboratory Name	Provided Current SGC Method	Participate in the Study
ID	Moscow	Anatek Labs, Inc - Moscow	x	x
OR	Tigard	Apex Laboratories, LLC	x	x
OR	Clackamas	Specialty Analytical		x
WA	Kirkland	Accu Laboratory, LLC		
WA	Everett	ALS Environmental - Everett	x	x
WA	Kelso	ALS Environmental - Kelso	x	
WA	Kirkland	AmTest Laboratories		
WA	Tukwila	Analytical Resources, LLC	x	
WA	Spokane	Anatek Labs, Inc - Spokane		
WA	Tukwila	Applied Analytical Services, NW		
WA	Vancouver	BSK Associates - Vancouver		
WA	Burlington	Edge Analytical, Incorporated	x	
WA	Tacoma	Eurofins Seattle	x	
WA	Spokane Valley	Eurofins Spokane	x	
WA	Ferndale	Exact Scientific Services, Inc.	x	x
WA	Seattle	Fremont Analytical, Inc.		
WA	Seattle	Friedman & Bruya, Inc.	x	x
WA	Seattle	King County Environmental Laboratory	x	
WA	Olympia	Libby Environmental, Inc.		
WA	Port Orchard	Manchester Environmental Lab	x	x
WA	Redmond	OnSite Environmental, Inc.	x	x
WA	Tacoma	Tacoma Environmental Services Laboratory		
WA	Tacoma	Water Management Laboratories, Inc.		

SGC = silica gel cleanup.

Silica Gel Cleanup

Current Lab Methods

The NWPTH-Dx method, as described in Ecology (1997), was written by Bob Carrell (Manchester Environmental Laboratory) and was based on Oregon's Department of Environmental Quality TPH-D and Washington's Department of Ecology WTPH-D methods. The SGC protocol for water is as follows:

> "In those cases where samples contain a significant amount of naturally occurring non-petroleum organics, e.g. leaf litter, bark, etc., which may contribute biogenic interferences, the following cleanup technique may be employed to assist in their reduction or elimination. Transfer the 10 mL sample extract to a 10 to 15 mL centrifuge tube, add 1 mL of concentrated sulfuric acid to the extract and stopper the tube. Mix thoroughly for 1 minute by either shaking the tube or with the use of a vortex-genie adjusted to the highest setting.

> Allow the two phases to separate. Centrifugation can be used to facilitate this process. Using a disposable glass pipet, transfer the methylene chloride (top) phase to another centrifuge tube and add approximately 0.4 grams (roughly equivalent to 1 mL of volume) of silica gel to the tube, stopper and mix as before. Allow the silica gel to settle or centrifuge. Repeat the sulfuric acid/silica gel cleanup once more. Transfer a portion of the extract to a 2 mL autosampler vial equipped with a Teflon-lined cap and store the extract in a refrigerator until analyzed. A smaller aliquot of the extract may be used for this cleanup procedure as long as the ratio of extract to acid/silica gel is maintained.

> It has been noted that some petroleum products, i.e. heavy fuel oils such as #6 fuel oil or Bunker-C, may experience a concentration loss of between 10 and 20 percent when subjected to this cleanup technique. This loss appears to be primarily associated with the removal of petroleum compounds which contain sulfur. To account for this loss when analyzing samples that have been subjected to the cleanup procedure in preparation for heavy fuel oil determination, the analyst must use utilize standards which have undergone the cleanup technique to calibrate the GC." (pg.19)

In many cases involving weathered DRO, identifying the chromatogram ranges or retention time range includes an unresolvable mixture of compounds (Figure 1). In this case, the analyst must, "at a minimum, include any unresolved envelope of compounds as well as all discrete component peaks with an area greater than or equal to 10% of the largest peak" (pg.25).
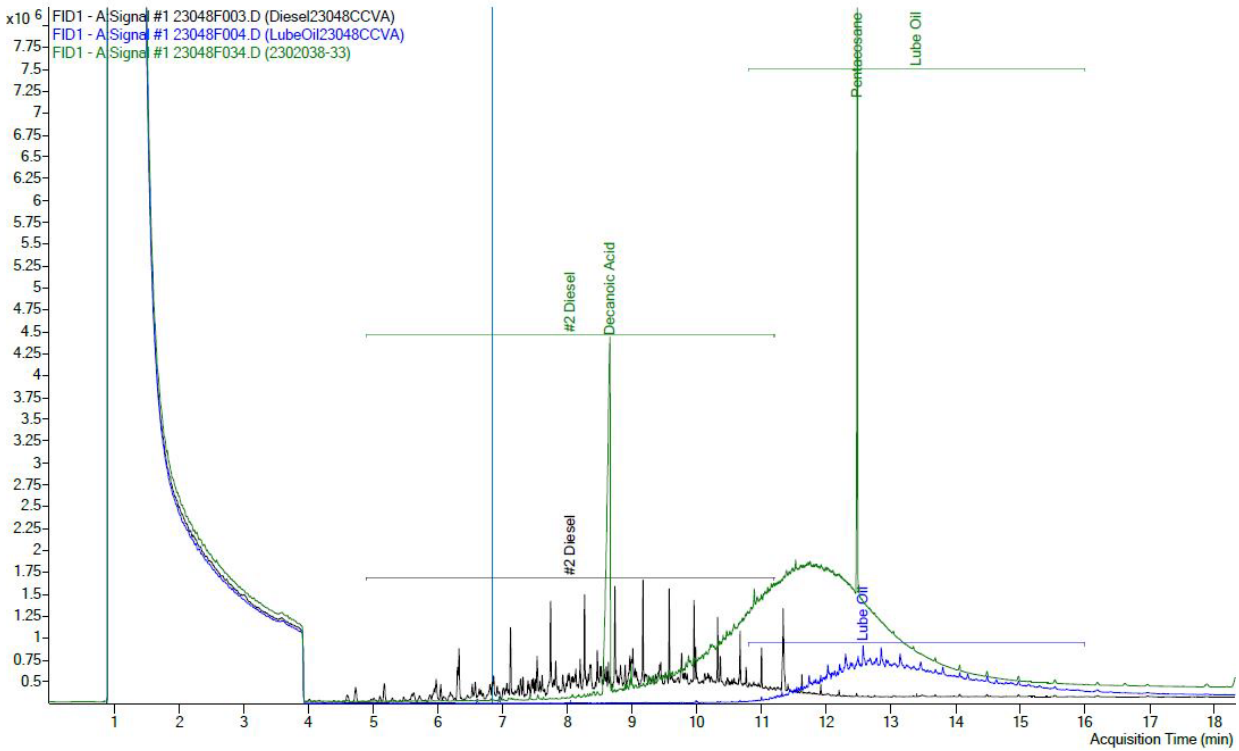
Figure 1. Example chromatogram of an unresolved complex mixture overlapping the DRO and RRO range.

The diesel range organics (DRO) range is shown in black with diesel #2 standard, the residual range organics (RRO) range is shown in blue with the Lube Oil standard, and the sample is shown in green.

Regional Lab Survey

All accredited labs were surveyed to ascertain whether they used an SGC protocol and what approach they used. There was a great deal of variability in the protocols used by the 13 labs that provided details on SGC (Table 2). Roughly half of the labs also used the sulfuric acid step of the protocol outlined in the NWTPH method (Ecology 1997). The amounts of silica used and whether it was free-flowing or packed in a column varied. The variability in how labs carry out the SGC step can potentially affect the reported concentrations of DRO.

All labs use a Gas Chromatography-Flame Ionization Detection (GC FID) instrument to measure DRO and similar extraction methods, solvents, and surrogate standards (Table A-1). Practical Quantitation Limits (PQL) for the analysis ranged from 0.05 – 0.5 mg/L.

Table 2. Current silica gel cleanup approach used by some regional accredited labs.

Laboratory	Method	Silica Gel	H$_2$SO$_4$ Used	Free-Flowing Si	SPE/Si Cartridge	Si Column	Si Column Amount	Amount of Extract Cleaned (ml)	DRO PQL (mg/L)
Manchester Environmental Lab (Ecology)	NWTPH-Dx	60–200 mesh activated silica gel	Used when requested	Yes (100 mg)	N/A	N/A	N/A	0.9 mL	0.15
OnSite Environmental, Inc.	Method 3630C	Silica gel, AR grade, 63–200 mesh	Yes, with SGC	No	N/A	Pasteur pipette	0.1 g	1	0.2
Friedman & Bruya, Inc.	NWTPH-Dx	Silica Gel 60	Not used	No	N/A	Pasteur Pipette	0.8 g	1 mL	0.05
Eurofins (TestAmerica Seattle-Tacoma)	Method 3630C	60–100 mesh activated silica gel	Not used	No	N/A	Pasteur pipette	Fill a 5 ¾" pasteur pipette	2–5	0.11
Eurofins (TestAmerica Seattle-Tacoma)	Method 3630C (Alaskan Samples)	60–100 mesh activated silica gel	Not used	No	N/A	6 mL glass reaction tube	1.00 g ± .05 g	1	0.11
Analytical Resources, Incorporated	NWTPH-Dx; Internal TI-011W	60–200 mesh activated silica gel	Possibly	Yes	N/A	N/A	0.04 g	1	0.1
Exact Scientific Services, Inc.	NWTPH-Dx	Silica gel 100–200 mesh	Yes, with SGC	Yes (100 mg silica in 2ml vial)	N/A	N/A	0.1 g	2	0.2
King County Environmental Laboratory	NWTPH-Dx	Silica gel 100–200 mesh	Yes, with SGC	No	N/A	Silica gel to a 5 mL pipet	0.8 g	2	0.2
Anatek Labs, Inc - Moscow	NWTPH-Dx	Silica gel 100–200 mesh	Possibly, upon request and if fatty acids are present	Yes (40ml VOA vial)	N/A	N/A	1–3 g	1	0.1
ALS Environmental - Everett	NWTPH-Dx	Silica gel	Yes, with SGC	Yes (2ml autosampler vial)	N/A	N/A	"About a pinch"	1	0.12
Edge Analytical, Incorporated	NWTPH-Dx	Not used "per Ecology's request"	Yes (0.3 ml)	Yes	N/A	N/A	0.04 g	1	0.05
Apex Laboratories, LLC	NWTPH-Dx	Unk	Yes with SGC	Yes (also column)	N/A	Unk	Unk	Unk	0.08

DRO = diesel range organics; N/A = not applicable; PQL = Practical Quantitation Limits; SPE = Solid Phase Extraction; Unk = unknown.

Field Methods

The same field site used in previous studies of weathered DRO (Hobbs et al. 2020) was used in this study. The groundwater well is large in diameter (10") and situated within an underground storage tank area on the sample site. The site was sampled on March 9, 2022.

The monitoring well was purged and sampled using industry-standard low-flow sampling techniques. The well was purged at a rate of less than 0.5 L/minute using dedicated tubing. Water levels were measured during the purging process to ensure the well was not over-pumped. For optimal sampling, the drawdown did not exceed 0.3 ft. Measurements were collected according to SOP EAP052 (Marti 2016a). The well was purged through a continuous flow cell until field parameters stabilized (pH, temperature, specific conductance, dissolved oxygen, and oxidation-reduction potential) as specified in SOP EAP078 (Marti 2016b). Measurement quality objectives are detailed in Table A-2.

As outlined in the study QAPP (Hobbs 2022), groundwater was sampled for a variety of chemical parameters to confirm that the overall chemistry had not changed significantly since the previous study. Groundwater was also collected in a large volume drum (30 gallons) lined with a Teflon bag for the subsequent method development and the inter-lab samples. Unfortunately, iron precipitated in the drum while in storage, and the DRO concentrations changed (decreased), necessitating an additional site visit to collect fresh samples. The well was re-sampled on February 1, 2023, for DRO only.

Each participating contract lab was sent triplicate samples, collected in two aliquots directly into 1L amber glass jars and acidified (preserved) on-site. Samples were stored on ice and were shipped on the day of sampling for analysis within the two-week hold time. Manchester Environmental Lab analyzed a total of ten samples.

Supplemental Parameters

As part of the initial analytical suite (3/9/22) for the groundwater samples, a number of supplemental parameters were measured to confirm that the sampled groundwater contained largely weathered DRO as the main contaminant. Lab methods and reporting limits are detailed in Table 3. All measurement quality objectives are detailed in Table A-3.

Table 3. Lab methods and reporting limits for supplemental parameters.

Analyte	Reporting Limit	Sample Prep Method	Analytical (Instrumental) Method
NWTPH-Gx	250 µg/L	SW5030B	NWTPH-Gx
BTEX [a]	1.0–2.0 µg/L	SW5030B	SW8021B
Polynuclear aromatic hydrocarbons [a]	0.05 µg/L	SW3510C	SW8270E w/SIM
Volatile petroleum hydrocarbons	50 µg/L	SW5030B	WDOE-VPH
Extractable petroleum hydrocarbons	40 µg/L	SW3510C	WDOE-EPH
Hardness	0.3 mg/L	N/A	SM2340B
Major cations [a]	0.025–0.25 mg/L	EPA 200.7	EPA 200.7
Major anions [a]	0.1–0.3 mg/L	N/A	EPA 300.0
Nitrate-nitrite	0.01 mg/L	N/A	SM4500-NO3I
Ammonia	0.01 mg/L	N/A	SM4500 NH3H
Dissolved organic carbon	0.5 mg/L	N/A	SM5310B

N/A = not applicable.
[a] reporting limits are compound-specific (see Table A-1).

Numerical Methods

Two main measures of precision were calculated: the repeatability standard deviation and the reproducibility standard deviation (ASTM 2019). The repeatability standard deviation, s_r is calculated using the following equation:

$$s_r = \sqrt{\sum_{1}^{p} s^2/p}$$

where:
s = the standard deviation,
p = the number of labs.

The reproducibility standard deviation, s_R, is calculated using the following equation:

$$s_R = \sqrt{s_L^2 + s_r^2}$$

where:
s_r = the repeatability standard deviation
s_L^2 = between-lab variance

To evaluate the measures of reproducibility and repeatability, the precision statistics were then compared with critical values of the between-lab and within-lab consistency to evaluate the method's performance. The critical values depend on the number of labs participating and the number of replicate samples taken.

The consistency statistic, h, indicates the between-laboratory consistency for a particular material. The average concentration from each lab is compared with the average of the other laboratories.

$$h = {}^d\!/_{s_{\bar{x}}}$$

where:

$d = \bar{x} - \bar{\bar{x}}$; the deviation of the lab average from the overall average

$s_{\bar{x}}$ = standard deviation of the lab averages

The consistency statistic, k, indicates how one laboratory's within-laboratory variability, compares with the variability across all the laboratories combined.

$$k = {}^s\!/_{s_r}$$

where:

s = standard deviation for one laboratory

s_r = repeatability standard deviation

Results and Discussion

Revised Silica Gel Cleanup Protocol

The revised SGC protocol is based on the EPA Method 3630 and the work of Zemo et al. (2013); the latter study compared the efficacy of free-flowing and Si column approaches, in addition to using a reverse surrogate during the procedure. Using a reverse surrogate allows the lab to track and establish quality assurance acceptance criteria for the removal of polar compounds that may interfere with the DRO results.

As a best practice, laboratories should pay particular attention to Section 8. Quality Control of Method 3630C. This section provides instructions for verifying the cleanliness and performance of the silica gel by analyzing reagent blank and recovery check samples. The verification samples and sample extracts being cleaned up using this method must be processed using the same procedures.

The revised SGC protocol was written to be cost-effective and easy to follow. The procedure is as follows:

1. Extract samples using your laboratory's typical process for NWTPH-Dx analysis, including spiking the samples with the typical surrogate used by your laboratory **AND** spiking with Decanoic Acid as a "reverse" surrogate to monitor the efficiency of the silica gel cleanup. (Suggested spike target concentration of approximately 250 ug/ml.) ***Please note: Spike the Decanoic Acid surrogate following extraction and prior to clean-up with silica gel.***

2. Analyze an untreated aliquot of the original sample extract according to the NWTPH-Dx method.

3. Select one of the following silica gel cleanup procedures:

    a. Treat sample and associated quality control sample (e.g., blanks, spikes, duplicates, and replicates) extracts with silica gel using purchased silica gel columns. A *suggested* prepacked column is the Supelco Supelclean™ LC-Si SPE Tube (part number 505048) with a 3 mL volume packed with 500 mg of silica gel. Rinse the silica gel in the column with up to 5 ml of methylene chloride and discard the rinsate. Place a concentrator tube or receiver at the bottom of the silica gel column. Add 1 ml of the sample extract into the silica gel column, and once the extract has almost reached the level of the silica gel, add 1 ml of methylene chloride to rinse the sample extract through the silica gel and allow to gravity filter completely through the column. If any solution remains in the column, gently push it through the column using a pipette bulb. Concentrate this extract to a 1 ml final volume.

    b. Treat sample and associated quality control sample (e.g., blanks, spikes, duplicates, and replicates) extracts with silica gel using self-packed silica gel columns. Using a 5 ¾ inch Pasteur pipet, add silica gel to approximately 3 cm of material in the column with a glass wool plug at the bottom. Rinse the silica gel in

the column with up to 5 ml of methylene chloride and discard the rinsate. Place a concentrator tube or receiver at the bottom of the silica gel column. Add 1 ml of the sample extract into the silica gel column. Once the extract has almost reached the level of the silica gel, add 1 ml of methylene chloride to rinse the sample extract through the silica gel and allow to gravity filter completely through the column. If any solution remains in the column, gently push it through the column using a pipette bulb. Concentrate this extract to a 1 ml final volume.

4. Analyze the cleaned extract according to the NWTPH-Dx method.

5. Report results for both treated and untreated extracts.

A flow chart of the recommended change in protocol from the original SGC steps is shown in Figure 2.
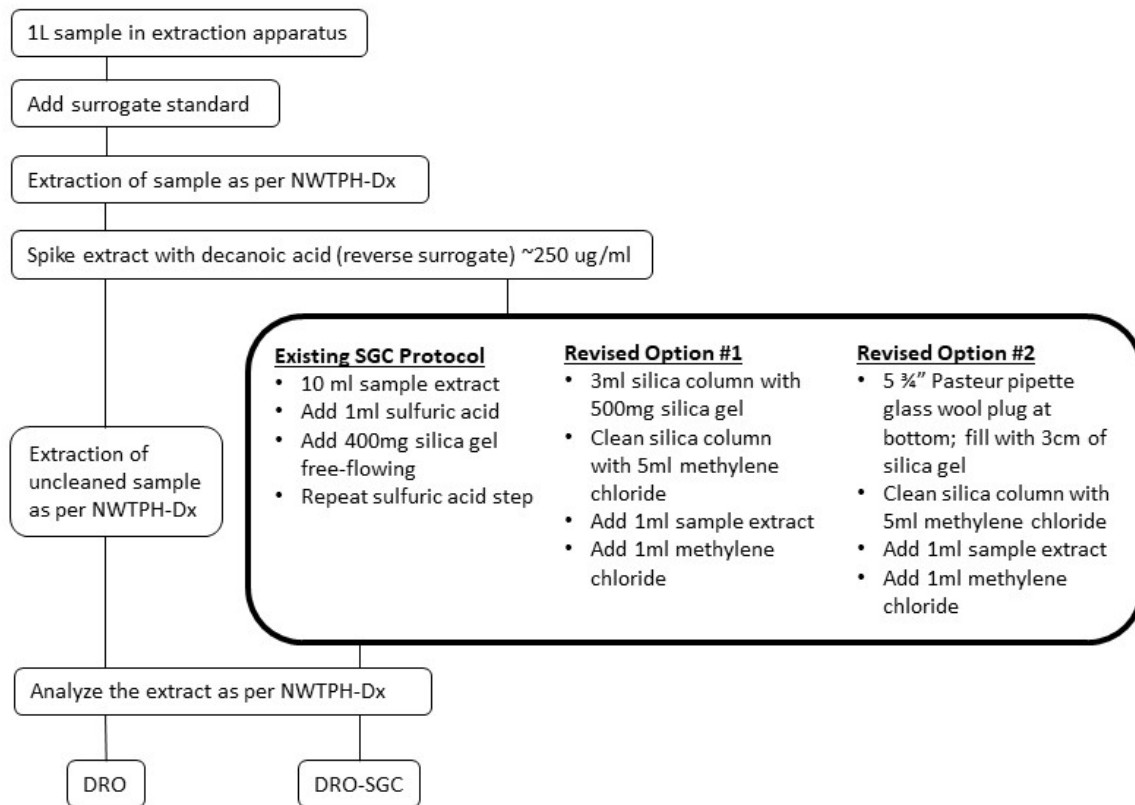
Figure 2. **Flow chart of the NWTPH-Dx method with revised silica gel cleanup (SGC) protocols.**

Accredited contract labs were offered the opportunity to comment and advise on the revised protocol and scope of work for the interlaboratory analysis. Only two labs provided comments, and we made minor changes to the protocol to accommodate one of the lab's comments.

The suggested quality objectives for the NWTPH-Dx analysis, including the recovery of the reverse surrogate, are detailed in Tables 4 – 6.

Table 4. Target Analyte List and Required Level of Quantitation.

NWTPH-Dx	PQL mg/L
Diesel Range Organics	0.15
Lube Oil (Residual Range Organics)	0.38

PQL = Practical Quantitation Limits.

Table 5. NWTPH-Dx Measurement Quality Objectives.

Analyte	Field Duplicates	Matrix Spike Duplicate	Lab Control Sample	Matrix Spikes	Surrogate Standards
#2 Diesel	<40% RPD	<40% RPD	70%–130%	70–130%	—
Lube Oil	<40% RPD	<40% RPD	70%–130%	70–130%	—
2-Fluorobiphenyl or o- or p-Terphenyl or Pentacosane	—	—	—	—	50%–150%
Decanoic Acid	—	—	—	—	0%–10%

RPD = relative percent difference.

Table 6. Laboratory Quality Control Sample Types and Frequencies.

Analyte	LCS	Method Blank	Lab Duplicate	Matrix Spikes
NWTPH-Dx	2/batch[1]	1/batch	2/batch	N/A

Note. Frequency for LCS (lab control sample) and lab duplicate is indicated as 2/batch to cover 1 untreated extract and 1 SGC (silica gel cleanup) extract.
LCS = lab control sample; N/A = not applicable.

Verification of SGC Protocol

The revised SGC protocol was tested on three samples collected in March 2022 (Table 7). The first two samples (DW3 and DW3 REP) were collected after the well was purged by a third-party consultant (Table A-4). Unfortunately, no detectable DRO was measured in these initial samples. The third sample was collected following further purging of the well by Ecology and stabilization of the field parameters (Table A-5). Concentrations of DRO in the third sample (DW-3 REP2) were measurable (Table 7) and comparable to the no-observed effects

concentration (NOEC) established in the previous study (Hobbs et al. 2020; 3.04 mg/L DRO), with groundwater from the same site.

Silica gel cleanup of the extract from the sample was conducted using three different approaches: (1) the original free-flowing method without the sulfuric acid step, (2) using a purchased silica gel column, and (3) using a lab-packed silica gel column. The free-flowing SGC protocol (1) reduced the measured DRO in the sample. However, the reverse surrogate (decanoic acid) suggested that a substantial amount of polar compounds remained in the sample (Table 7). Approaches 2 and 3 are options detailed in the revised SGC protocol. Both revised approaches performed similarly and reduced DRO to below the practical quantitation limit (PQL), and the reverse surrogate confirmed the removal of all polar compounds.

Concentrations of residual range organics (Lube Oil) were measurable in the DW-3 REP2 sample. A PQL of 0.2 mg/L was not met for the analysis; the method reporting limit (MRL) was 0.38 mg/L. Despite not removing all the polar compounds, the free-flowing SGC approach reduced the RRO concentration to less than the MRL. The revised SGC approaches also showed the RRO concentrations less than the MRL, with confirmation by the reverse surrogate, that all polar compounds were likely removed during the cleanup step.

Table 7. Results for the initial testing of the revised SGC protocol. Results in mg/L.

Sample ID	Date	Time	Lab ID	Analyte	Uncleaned	SGC (1)	SGC (2)	SGC (3)
DW-3	3/9/2022	10:30:00	2203054-01	DRO	0.32	0.15 U	0.15 U	0.15 U
DW-3	3/9/2022	10:30:00	2203054-01	RRO	0.54 U	0.38 U	0.38 U	0.38 U
DW-3	3/9/2022	10:30:00	2203054-01	Pentacosane	120	62	98	98
DW-3	3/9/2022	10:30:00	2203054-01	Decanoic Acid	127	17	0	0
DW-3 REP	3/9/2022	10:30:00	2203054-02	DRO	0.32 U	0.15 U	0.15 U	0.15 U
DW-3 REP	3/9/2022	10:30:00	2203054-02	RRO	0.54 U	0.38 U	0.38 U	0.38 U
DW-3 REP	3/9/2022	10:30:00	2203054-02	Pentacosane	117	105	105	96
DW-3 REP	3/9/2022	10:30:00	2203054-02	Decanoic Acid	120	25	0	0
DW-3 REP2	3/9/2022	12:30:00	2203054-04	DRO	3.4	0.8	0.2 U	0.24 U
DW-3 REP2	3/9/2022	12:30:00	2203054-04	RRO	3.73	0.42 U	0.38 U	0.38 U
DW-3 REP2	3/9/2022	12:30:00	2203054-04	Pentacosane	101	91	96	87
DW-3 REP2	3/9/2022	12:30:00	2203054-04	Decanoic Acid	121	45	0	0

DRO = diesel range organics (#2 Diesel); RRO = residual range organics (Lube Oil); SGC (1) = silica gel cleanup as per current NWTPH-Dx method (free flowing); SGC (2) = silica gel cleanup using purchased silica gel columns; SGC (3) = silica gel cleanup using lab pack silica gel columns; U = analyte not detected above the PQL (practical quantitation limit).

The supplemental parameters analyzed during the initial stages of the project confirmed that DRO was the principal contaminant present in the groundwater (Table A-6). This finding is similar to the previous study by Hobbs et al. (2020), which relied on the same groundwater source. The analytical QC for the supplemental parameters met all the acceptance criteria (Appendix B). During the data validation of the contract samples for extractable petroleum hydrocarbons (EPH), two QC samples had laboratory control standard recoveries and surrogate recoveries lower than the QAPP QC limits and were qualified. The results met the contract lab in-house control limit. All of the sample data was acceptable for use with qualifiers.

Inter-Laboratory Comparison of SGC Protocol

Sample water was initially collected in a large drum to be used for the inter-laboratory comparison, as per the project QAPP (Hobbs 2022). However, while in storage, the DRO concentrations decreased from 3.4 mg/L DRO to approximately 0.82 mg/L DRO (Table 8). We, therefore, deviated from the QAPP and resampled the groundwater, collecting sufficient sample splits in aliquots. All sample bottles were filled in two aliquots, and the pump rate was consistent throughout the filling of the bottles. The stabilization of the field parameters was documented according to the SOP (Table A-7).

Table 8. Re-analysis of groundwater sampled on March 9, 2022.

Sample ID	Date	Lab ID	Analyte	Uncleaned (mg/L)
EB1 (DW-3 REP2)	9/1/2022	2208099-01	#2 Diesel	0.87
EB1 (DW-3 REP2)	9/1/2022	2208099-01	Lube Oil	2.09
EB2 (DW-3 REP2)	9/1/2022	2208099-02	#2 Diesel	0.77
EB2 (DW-3 REP2)	9/1/2022	2208099-02	Lube Oil	1.99

Data Validation

All contract laboratories are hereafter referred to anonymously, except Ecology's Manchester Environmental Lab (MEL); the numbering of the labs does not reflect the list of labs in Table 1. MEL had detections of DRO in lab method blanks, but they were not above action levels (Appendix C; as a result, sample results for the DRO-SGC were qualified as "U" (below detection) despite being above the reporting limit or PQL of 0.15 mg/L.

The results from Lab 4 for both the DRO and the DRO-SGC analysis were rejected during the data validation stage (Appendix C). The laboratory lost a critical chemist during the project, and the lab could not fully recover the data for the project. The reported DRO untreated results were well below those of other laboratories due to the use of the sulfuric acid cleanup step as per the original NWTPH-Dx method (Ecology 1997), and there were deficiencies with batch QC and instrument calibration.

The efficiency of the SGC procedure was based on the results of the reverse surrogate (decanoic acid). Lab 4 did not use the reverse surrogate. The results from Lab 2 showed that 86% – 96% of the decanoic acid remained in the samples following the SGC step. The measurement quality

objective is 0% – 10% for the decanoic acid; therefore, cleanup was not achieved. The reported results for the DRO-SGC (cleaned samples) from Lab 2 were not considered in the calculations of method precision statistics. However, the results highlight the successful use of a reverse surrogate to evaluate cleanup efficiency.

Analytical Results

Ecology's Manchester Environmental Laboratory analyzed ten (10) replicates of the sample groundwater (Table 9). Each contract lab received triplicate samples for the analysis of NWTPH-Dx with and without SGC, using the revised protocol. Following the cleanup of the sample extracts using the revised SGC protocol, most results were near the reporting limit of 0.15 mg/L or were qualified as "U — below detection" (Table 9). Using the reverse surrogate, decanoic acid worked well and showed the removal of polar compounds. Labs 3 and 5 through 7 had concentrations of DRO-SGC similar to MEL's and near the PQL (Figure 3). Lab1 had minor amounts of detectable DRO following the SGC. As mentioned earlier, the DRO-SGC results for Lab 2 were rejected due to insufficient sample cleaning.

Table 9. DRO and DRO-SGC results and surrogate recoveries for all labs

Lab	Sample ID	DRO (mg/L)	DRO-SGC	RRO	RRO-SGC	DA (%)	DA-SGC (%)	DRO (Rec %)	DRO-SGC (Rec %)	Surrogate
MEL	DW3-A	4.06	0.4 U	9.76	0.38 U	138	0	132	109	Pentacosane
MEL	DW3-B	3.69	0.41 U	9.42	0.37 U	129	0	133	120	Pentacosane
MEL	DW3-C	3.75	0.4 U	10.1	0.38 U	132	0	139	130	Pentacosane
MEL	DW3-D	3.59	0.38 U	10.1	0.38 U	133	0	137	122	Pentacosane
MEL	DW3-E	3.35	0.38 U	9.37	0.38 U	125	0	132	116	Pentacosane
MEL	DW3-F	3.13	0.39 U	9.02	0.37 U	120	0	130	114	Pentacosane
MEL	DW3-G	3.15	0.36 U	8.96	0.38 U	124	0	130	107	Pentacosane
MEL	DW3-H	3.13	0.36 U	8.8	0.38 U	121	0	128	113	Pentacosane
MEL	DW3-I	3.19	0.38 U	9.21	0.38 U	120	0	132	107	Pentacosane
MEL	DW3-J	2.89	0.35 U	8.51	0.38 U	113	0	128	110	Pentacosane
Lab 1	DW3-A	5.00	0.74	1.40	0.25 U	NA	1.5	112	124	Pentacosane
Lab 1	DW3-B	4.90	0.70	1.40	0.25 U	NA	1.5	107	119	Pentacosane
Lab 1	DW3-C	4.60	0.67	1.40	0.25 U	NA	1.5	98.7	110	Pentacosane
Lab 2	DW3-A	3.81 J	1.98 J	0.21 UJ	0.21 UJ	NA	96.1 J	85.1	93.7	Terphenyl-d14
Lab 2	DW3-B	3.54 J	1.89 J	0.20 UJ	0.20 UJ	NA	94.2 J	87.4	92.7	Terphenyl-d14
Lab 2	DW3-C	2.27 J	1.33 J	0.20 UJ	0.20 UJ	NA	86.2 J	88	100	Terphenyl-d14
Lab 3	DW3-A	2.55	0.13 J	0.16 U	0.16 U	NA	0	81	73	o-Terphenyl
Lab 3	DW3-B	2.97	0.12 J	0.16 U	0.16 U	NA	0	76	72	o-Terphenyl
Lab 3	DW3-C	2.90	0.15 J	0.16 U	0.16 U	NA	0	87	76	o-Terphenyl
Lab 4	DW3-A	0.30 R	0.15 R	0.4 R	0.24 R	NA	NA	98	73	o-Terphenyl
Lab 4	DW3-B	0.28 R	0.16 R	0.41 R	0.24 R	NA	NA	113	86	o-Terphenyl
Lab 4	DW3-C	0.25 R	0.14 R	0.27 R	0.2 R	NA	NA	112	67	o-Terphenyl
Lab 5	DW3-A	4.70	0.24	2.50	0.04 U	NA	2	83	99	o-Terphenyl
Lab 5	DW3-B	4.60	0.23	2.60	0.04 U	NA	2	81	82	o-Terphenyl
Lab 5	DW3-C	5.00	0.26	3.10	0.04 U	NA	2	88	90	o-Terphenyl
Lab 6	DW3-A	4.20	0.18	4.20	0.16 U	112	0	108	101	o-Terphenyl
Lab 6	DW3-B	4.20	0.16	4.20	0.16 U	115	0	105	95	o-Terphenyl

Lab	Sample ID	DRO (mg/L)	DRO-SGC	RRO	RRO-SGC	DA (%)	DA-SGC (%)	DRO (Rec %)	DRO-SGC (Rec %)	Surrogate
Lab 6	DW3-C	4.00	0.17	3.90	0.15 U	113	0	108	98	o-Terphenyl
Lab 7	DW3-A	2.55	0.55	2.74	0.14	NA	0	120	122	o-Terphenyl
Lab 7	DW3-B	2.54	0.62	3.34	0.47	NA	0	115	134	o-Terphenyl
Lab 7	DW3-C	1.03	0.28	1.89	0.32	NA	0	52.8	73.6	o-Terphenyl

DRO = diesel range organics; DRO-SGC = diesel range organics-silica gel cleanup; RRO = residual range organics; RRO-SGC = residual range organics-silica gel cleanup; DA = decanoic acid; DA-SGC = decanoic acid following silica gel cleanup; DRO (Rec %) = diesel range organics surrogate recovery;
DRO-SGC (Rec %) = diesel range organics-silica gel cleanup surrogate recovery; N/A = not applicable; Qualifiers: U = analyte not detected above the PQL,
J = analyte detected but the result is an estimate, R = result rejected.

An analysis of variance was conducted among the labs with a Tukey-Kramer post-hoc test for significant differences among means with unequal sample sizes (Figure 3). Labs 2, 3, and 6 were not significantly different from the MEL results for DRO (uncleaned), whereas 1, 5, and 7 were significantly different at a 95% confidence level.
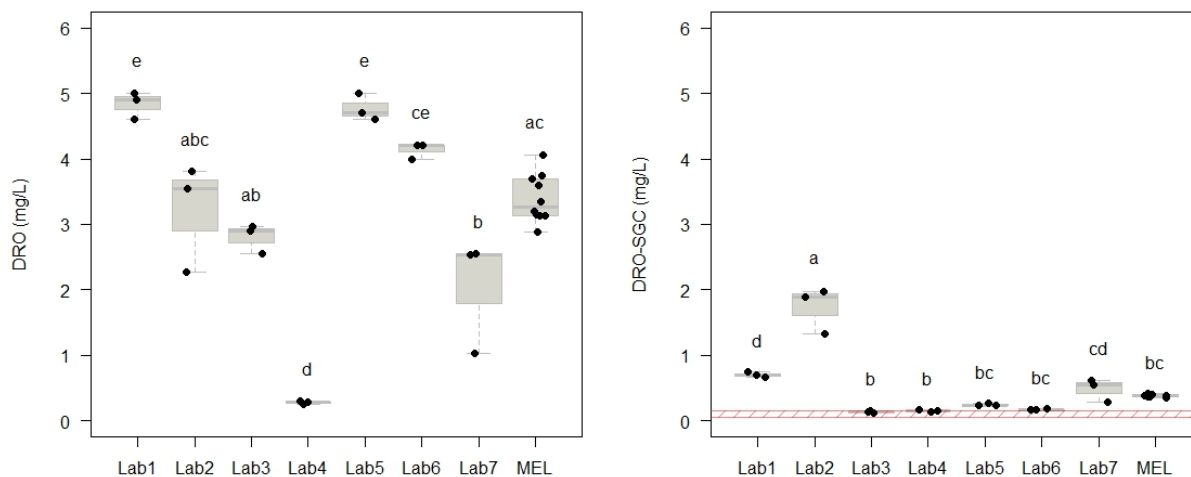
Figure 3. Scatterplot of uncleaned (DRO) and cleaned (DRO-SGC) samples.
Box and whisker plots of the same data for each lab are shown in the background. The red dashed area on the right plot is the PQL range of the labs. Different letters above the boxes signify statistical significance between groups (labs) at the level of $\alpha = 0.05$, in accordance with the ANOVA and post-hoc tests.

The chromatogram of the DRO was characteristic of an unresolved complex mixture (Figure 4). The reduction of the instrument response following the SGC and the removal of polar compounds is visible on the chromatogram. All labs identified the petroleum as an unresolved complex mixture (Figure A-1 to A-7). This is consistent with the previous study of weathered DRO at the sample site (Hobbs et al. 2020).
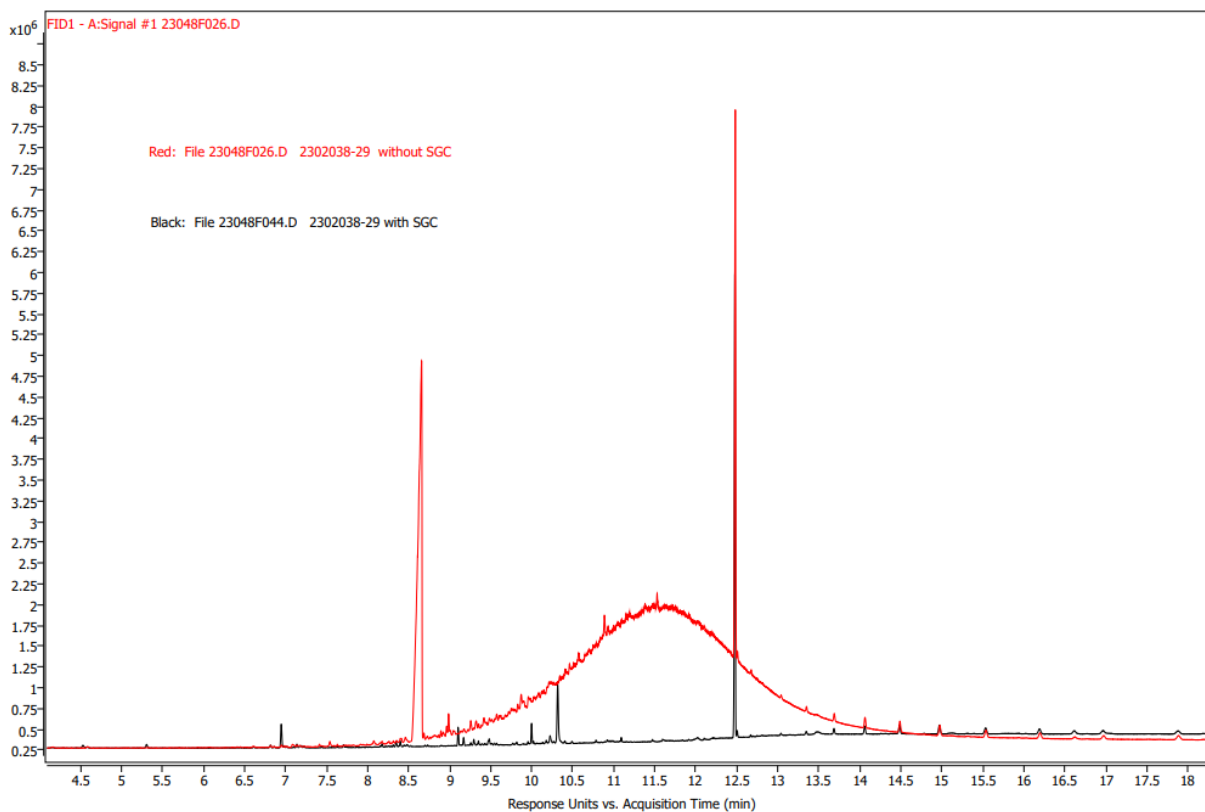
Figure 4. Chromatogram of DRO with and without SGC.
Sample 2302038-29 (DW3-A) was analyzed at Manchester Environmental Laboratory. The red line is the response curve for the uncleaned sample, and the black line is the response curve for the sample following SGC.

RRO results were variable among the labs (Figure A-8). Labs 2 – 4 did not detect or report any quantifiable RRO, whereas MEL reported a mean concentration of 9.33 mg/L (Table 9). All labs used standards for diesel #2 and Lube Oil to calibrate, and since the unresolved mixture was neither of these products, the accuracy of the reported RRO concentration varied greatly because it did not match the standard range. The NWTPH-Dx method does not rely on specific carbon ranges for quantification; instead, it is based on the retention times of the hydrocarbon standards. Furthermore, the standards are not weathered polar compounds, which are often a component in environmental samples. The analytical reality of the NWTPH-Dx method has some inherent level of subjectivity from the laboratory chemist, especially when quantifying overlapping carbon ranges at low concentrations.

SGC Precision

The precision of the interlaboratory samples and the revised procedure were assessed following ASTM protocols (ASTM 2019). To assess the consistency of the results among and within the contract labs, we calculated two consistency statistics (Table 10): the *h*-statistic indicates the between-laboratory consistency, and the *k*-statistic indicates the within-lab consistency. Both *h* and *k* have critical values based on the number of labs and replicates (ASTM 2019). In general, the uncleaned DRO results and the SGC-cleaned DRO results had acceptable consistency (*h*-

statistic) among the labs. Lab1 had higher values of the *h*-statistic for DRO and DRO-SGC analysis, and Lab 7 had higher *h*-statistic values for the DRO analysis. Lab7 had a *k*-statistic above the critical value for the DRO-SGC analysis, indicating a high variability among replicate samples at this lab. It's worth noting that Lab7 reported DRO-SGC concentrations just above and within five times the PQL; higher variability among replicates at very low concentrations is generally not a cause for rejecting results. Overall, the consistency of the DRO and DRO with the revised SGC cleanup was acceptable, suggesting that the revised silica gel cleanup protocol would give consistent results among labs.

Table 10. Consistency statistics for all laboratories for both DRO and DRO-SGC.

Laboratory	DRO (h)	DRO (k)	DRO-SGC (h)	DRO-SGC (k)
Lab1	1.06	0.40	1.48	0.43
Lab2	-0.38	1.60	N/A	N/A
Lab3	-0.73	0.44	-0.89	0.19
Lab5	1.01	0.40	-0.43	0.19
Lab6	0.44	0.22	-0.73	0.12
Lab7	-1.41	1.70	0.57	**2.18**
MEL	-0.20	0.68	0.13	0.24
Critical values[a]	±1.92	<1.98	±1.74	<1.92

Note. Values above the critical value are bold.
[a] Critical values taken from ASTM 2019.

The goal of assessing the precision of the SGC procedure in an interlaboratory comparison was to provide some metrics of precision for the revised protocol that may or may not be used for future comparison or evaluation of results. The use of the terms reproducibility and repeatability is consistent with the ASTM Standard E177 (ASTM 2020), which defines the standard practice for terms under a method statement of precision. We generated precision statistics on the external laboratory data (Table 11). Should the revised silica gel cleanup protocol be adopted by regionally accredited labs in the future, it may be useful to revisit the evaluation of reproducibility and repeatability statistics with a larger number of participating labs.

Table 11. Precision statistics for the analysis of DRO and DRO with SGC

DRO	DRO-SGC	Precision Statistics	Description
3.60	0.35	$\bar{\bar{x}}$	Average of lab averages
1.03	0.22	$s_{\bar{x}}$	Standard deviation of lab averages
0.54	0.08	s_r	Repeatability standard deviation
0.98	0.04	s_L	Between-laboratory standard deviation
1.11	0.09	s_R	Reproducibility standard deviation
1.50	0.23	r	Repeatability limit
3.12	0.26	R	Reproducibility limit

DRO = diesel range organics; DRO-SGC = diesel range organics - silica gel cleanup.

Conclusions

After a survey of regional laboratories, it is apparent that there is variability in how Ecology-accredited laboratories are currently using the 1997 SGC protocol under the NWTPH-Dx method. This variability could affect reported results for diesel range organics.

Ecology wrote a revised SGC protocol that was tested internally at Ecology's Manchester Environmental Laboratory. The revised protocol no longer uses a sulfuric acid step. There are two options for using silica gel columns, and the revised protocol relies on a reverse surrogate to evaluate the efficacy of the cleanup. Ecology-accredited labs were asked to comment on the revised protocol; two labs provided feedback. Seven contract labs participated in a paid inter-laboratory study to evaluate the repeatability and reproducibility of the revised SGC protocol. Triplicate samples were analyzed.

The results of this inter-laboratory study support the following conclusions:

- Repeatability and reproducibility statistics typical of inter-laboratory studies were within acceptance thresholds for the uncleaned extracts (DRO). There were statistically significant differences among the lab-reported DRO results, which reflects the variability within the NWTPH-Dx method.
- Six labs successfully carried out the revised SGC protocol and reported DRO-SGC results for the cleaned extracts. The use of the reverse surrogate showed that one of the labs did not remove all polar compounds, and the lab reported detectable DRO in the cleaned sample. Repeatability and reproducibility statistics for the DRO-SGC results were within acceptance thresholds, except for one lab that had higher within-lab variability.
- The revised SGC protocol is acceptable for use in the NWTPH-Dx method.

Recommendations

Following the successful revision of the Silica Gel Cleanup (SGC) protocol under the NWTPH-Dx method, the following recommendations can be made:

- The SGC protocol should be incorporated into the NWTPH-Dx method guidance and disseminated to all labs accredited by Ecology for the NWTPH-Dx method.
- Toxics Cleanup Program site managers should be aware of this revised protocol and recommend its use in future cleanup projects involving DRO in groundwater.

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Glossary, Acronyms, and Abbreviations

Glossary

Practical Quantitation Limit (PQL): The analyte concentration selected as the lowest non-zero standard in the instrument calibration curve, adjusted for sample specific conditions (e.g.: sample size, percent solids, dilutions, cleanup procedures, etc.). Results below the PQL are considered less accurate and are qualified as estimates.

Precision: the closeness of agreement between independent test results obtained under stipulated conditions.

Repeatability: precision of test results from tests conducted within the shortest practical time period on identical material by the same test method in a single laboratory with all known sources of variability conditions controlled at the same levels.

Repeatability limit (r): the value below which the absolute difference between two individual test results obtained under repeatability conditions may be expected to occur with a probability of approximately 0.95 (95 %).

Repeatability standard deviation (s_r): the standard deviation of test results obtained under repeatability condition.

Repeatability variance, s_r^2: the sample variance of test results obtained under repeatability conditions. This statistic is estimated for a material as the pooled within-laboratory variances over all of the laboratories in the ILS.

Reproducibility: precision of test results from tests conducted on identical material by the same test method in different laboratories.

Reproducibility limit (R): the value below which the absolute difference between two test results obtained under reproducibility conditions may be expected to occur with a probability of approximately 0.95 (95 %).

Reproducibility standard deviation (s_R): the standard deviation of test results obtained under reproducibility conditions.

Reproducibility variance, s_R^2: the sample variance of test results obtained under reproducibility conditions. This statistic is estimated as the sum of the two variance components due to between-laboratories, s_L^2, and within-laboratories, s_r^2 .

Reverse surrogate: A surrogate is a chemical, similar to the compounds of interest, spiked into the environmental samples prior to preparation and analysis, intended to evaluate the extraction procedure and matrix interference. The reverse surrogate is spiked into the sample following preparation but prior to analysis and is intended to evaluate the cleanup or removal of interferences.

Acronyms and Abbreviations

DO	Dissolved oxygen
DRO	Diesel Range Organics
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
ILS	Inter-Laboratory Study
MDL	Method detection limit
MEL	Manchester Environmental Laboratory
NWTPH-Gx	Northwest Total Petroleum Hydrocarbons — Gasoline fraction
NWTPH-Dx	Northwest Total Petroleum Hydrocarbons — Diesel fraction
ORP	Oxidation Reduction Potential
PQL	Practical quantitation limit
RPD	Relative percent difference
RRO	Residual Range Organics
RSD	Relative standard deviation
SGC	Silica gel cleanup
Sp Cond	Specific conductance
WAC	Washington Administrative Code

Units of Measurement

°C	degrees centigrade
dw	dry weight
g	gram, a unit of mass
mg	milligram
mg/L	milligrams per liter (parts per million)
μg/L	micrograms per liter (parts per billion)

Appendices

Appendix A. Methods, Quality Objectives and Results

Table A-1. NWTPH methods for non-potable waters used by regional accredited labs.

Lab	Instrument (GC FID)	Extraction Method	DRO Extraction Solvent	Spiking Compound	Surrogate Standard	PQL Water (mg/L)	Mean % Recovery (20 runs)	SD % Recovery (20 runs)
OnSite Environmental, Inc.	AT 7890A GC System — dual autosamplers	Method 3510C; Separatory Funnel	Methylene Chloride	#2 Diesel Oil	—	0.2	100.9	6.5
Friedman & Bruya, Inc.	Agilent 5890, 6890, 8890	Separatory Funnel, SW3510C	Methylene Chloride	#2 Diesel Oil	Pentacosane	0.5	96.4	9.343729
Eurofins (TestAmerica Seattle-Tacoma)	Agilent 6890 or 7890 GC with FID	Separatory Funnel, SW3510C	Methylene Chloride	#2 Diesel Oil	o-Terphenyl	0.11	81.98	9.16
Eurofins (TestAmerica Seattle-Tacoma)								
Analytical Resources, Incorporated	Unk	Separatory Funnel, SW3510C	Methylene Chloride	#2 Diesel Oil	o-Terphenyl	0.1	102	12.6
Exact Scientific Services, Inc.	Agilent 7890 GC-FID, Restek: Rxi-5ms column 30m	Separatory Funnel, SW3510C	Methylene Chloride	#2 Diesel Oil	o-Terphenyl	0.2	86.6	13.1
King County Environmental Laboratory	Agilent 8890 GC with FID	Continuous Liquid-Liquid, SW-846 3520C	Methylene Chloride	#2 Diesel Oil restek # 31259, Motor Oil SAE 30W restek # 54367 (custom mix)	Pentacosane, 2-Fluorobiphenol	0.2	96.8	4.7
Anatek Labs, Inc — Moscow	HP 6890 with ZB-5 M5 Plus capillary 0.25 mm ID column 30m	Separatory Funnel, SW3510C or Liquid-Liquid, SW-846 3520C	Methylene Chloride	#2 Diesel Oil restek # 31259, Motor Oil SAE 30W restek # 54367 (custom mix)	Pentacosane	0.1	92.2	11
ALS Environmental — Everett	Agilent 7890 GC with FID	Separatory Funnel, SW3510C	Methylene Chloride	#2 Diesel Oil	Pentacosane	0.12	~98	N/A
Edge Analytical, Incorporated	Agilent 8890 GC with FID	Separatory Funnel, SW3510C	Methylene Chloride	#2 Diesel Oil	o-Terphenyl	0.05	95.8	18.6
Apex Laboratories, LLC	6890 dual FIDs	Separatory Funnel, SW3510C	Methylene Chloride	#2 Diesel Oil	o-Terphenyl	0.08	90.5	7.51

DRO = diesel range organics; N/A = not applicable; PQL = practical quantitation limit; SD = standard deviation; Unk = unknown.

Table A-2. Measurement quality objectives for Hydrolab calibration checks.

Parameter	Units	Accept	Qualify	Reject
pH	std. units	≤0.2	>0.2 and ≤0.8	>0.8
Conductivity[a]	µS/cm	≤5%	>5% and ≤15%	>15%
Temperature	°C	≤0.2	>0.2 and ≤0.8	>0.8
Dissolved Oxygen	mg/L	≤0.3	>0.3 and ≤0.8	>0.8

Note. Values indicate the difference, shown as absolute or percentage values, between measured and calibrated values.

[a] Criteria are expressed as a percentage of readings. For example, buffer = 100.2 µS/cm and Hydrolab = 98.7 µS/cm; (100.2 - 98.7)/100.2 = 1.49% variation, which would fall into the acceptable data criterion of less than 5%.

Table A-3. Measurement quality objectives for water chemistry.

Parameter	Analyte Group	Field Duplicate Samples (RPD)	Matrix Spike-Duplicates (RPD)	Verification Standards (LCS) (%)	Matrix Spikes (%)	Surrogate Standards[a] (%)	Reporting Limit
NWTPH-Dx (DRO)[b]	Organics	<40%	<40%	70%–130%	70%–130%	50%–150%	0.15 mg/L
NWTPH-Gx (GRO)[c]	Organics	<50%	<40%	70%–130%	70%–130%	70%–130%	0.07 mg/L
Volatile petroleum hydrocarbons (VPH)	Organics	<30%	<30%	70%–130%	70%–130%	70%–130%	50 µg/L
Extractable petroleum hydrocarbons (EPH)	Organics	<30%	<30%	70%–130%	70%–130%	70%–130%	40 µg/L
Benzene	Organics	<50%	<50%	70%–130%	70%–130%	70%–130%	1.0 µg/L
Ethylbenzene	Organics	<50%	<50%	70%–130%	70%–130%	70%–130%	1.0 µg/L
Toluene	Organics	<50%	<50%	70%–130%	70%–130%	70%–130%	1.0 µg/L
Xylenes	Organics	<50%	<50%	70%–130%	70%–130%	70%–130%	2.0 µg/L
1-Methylnaphthalene	PAHs	<50%	<40%	41%–117%	39%–113%	N/A	0.05 µg/L
2-Chloronaphthalene	PAHs	<50%	<40%	50%–150%	50%–150%	N/A	0.05 µg/L
2-Methylnaphthalene	PAHs	<50%	<40%	36%–112%	34%–105%	N/A	0.05 µg/L
Acenaphthene	PAHs	<50%	<40%	40%–112%	55%–97%	N/A	0.05 µg/L
Acenaphthylene	PAHs	<50%	<40%	10%–126%	48%–103%	11%–139%	0.05 µg/L
Anthracene	PAHs	<50%	<40%	24%–127%	51%–113%	27%–132%	0.05 µg/L
Benzo(a)anthracene	PAHs	<50%	<40%	38%–147%	59%–137%	N/A	0.05 µg/L
Benzo(a)pyrene	PAHs	<50%	<40%	14%–129%	42%–110%	29%–120%	0.05 µg/L
Benzo(b)fluoranthene	PAHs	<50%	<40%	42%–133%	53%–99%	N/A	0.05 µg/L
Benzo(g,h,i)perylene	PAHs	<50%	<40%	12%–122%	38%–131%	N/A	0.05 µg/L
Benzo(k)fluoranthene	PAHs	<50%	<40%	38%–131%	33%–122%	N/A	0.05 µg/L
Carbazole	PAHs	<50%	<40%	42%–133%	63%–123%	N/A	0.05 µg/L
Chrysene	PAHs	<50%	<40%	37%–128%	51%–116%	N/A	0.05 µg/L
Dibenzo(a,h)anthracene	PAHs	<50%	<40%	10%–134%	27%–129%	N/A	0.05 µg/L
Dibenzofuran	PAHs	<50%	<40%	39%–121%	47%–105%	N/A	0.05 µg/L
Fluoranthene	PAHs	<50%	<40%	42%–123%	60%–107%	N/A	0.05 µg/L
Fluorene	PAHs	<50%	<40%	50%–150%	50%–150%	43%–112%	0.05 µg/L
Indeno(1,2,3-cd)pyrene	PAHs	<50%	<40%	29%–129%	37%–135%	N/A	0.05 µg/L
Naphthalene	PAHs	<50%	<40%	41%–105%	41%–97%	N/A	0.05 µg/L
Phenanthrene	PAHs	<50%	<40%	18%–105%	18%–105%	N/A	0.05 µg/L
Pyrene	PAHs	<50%	<40%	43%–131%	61%–118%	48%–143%	0.05 µg/L
Retene	PAHs	<50%	<40%	10%–151%	57%–139%	N/A	0.05 µg/L
Sodium	Major ions	<20%	<20%	85%–115%	75%–125%	N/A	0.025 mg/L

Parameter	Analyte Group	Field Duplicate Samples (RPD)	Matrix Spike-Duplicates (RPD)	Verification Standards (LCS) (%)	Matrix Spikes (%)	Surrogate Standards[a] (%)	Reporting Limit
Magnesium	Major ions	<20%	<20%	85%–115%	75%–125%	N/A	0.025 mg/L
Potassium	Major ions	<20%	<20%	85%–115%	75%–125%	N/A	0.25 mg/L
Calcium	Major ions	<20%	<20%	85%–115%	75%–125%	N/A	0.025 mg/L
Sulfate	Major ions	<20%	<20%	90%–110%	75%–125%	N/A	0.30 mg/L
Chloride	Major ions	<20%	<20%	90%–110%	75%–125%	N/A	0.10 mg/L
Bromide	Major ions	<20%	<20%	90%–110%	75%–125%	N/A	0.10 mg/L
Fluoride	Major ions	<20%	<20%	90%–110%	75%–125%	N/A	0.10 mg/L
Sulfides	Major ions	<20%	<20%	75%–125%	75%–120%	N/A	0.05 mg/L
Ammonia	Nutrients	<20%	<20%	80%–120%	75%–125%	N/A	0.01 mg/L
Nitrate-nitrite	Nutrients	<20%	<20%	85%–115%	75%–125%	N/A	0.01 mg/L
Dissolved organic carbon	Nutrients	<20%	<20%	80%–120%	75%–125%	N/A	0.5 mg/L

LCS = Lab Control Sample; N/A = not applicable ; RPD = relative percent difference; PAHs = polycyclic aromatic hydrocarbons.
[a] Surrogate recoveries are compound-specific.
[b] Based on the analysis of #2 Diesel (CAS#: 68476-34-6).
[c] Based on the analysis of gasoline (CAS#: 86290-81-5).

Table A-4. Initial field parameters measured during well purging on March 9, 2022.

Time	Temp (deg C)	DO (mg/L)	Sp Cond (uS/cm)	pH	ORP (mV)	Water Level
9:10	10	8.74	1349	6.22	125.8	7.35
9:15	10	7.05	1319	6.43	121.2	7.35
9:20	10.1	6.93	1297	4.62	119.1	7.35
9:25	10.1	6.77	1296	6.58	118	7.35

Note. Well diameter is 12", well depth is 11.6", peristaltic pump was used at a depth of 8' and a rate of 220 ml/min; static water level was 7.35'. Purge water was clear with an earthy odor.
DO = dissolved oxygen; ORP = oxidation/redox potential; Sp Cond = specific conductance.

Table A-5. Final field parameters measured during well purging on March 9, 2022.

Time	Temp (deg C)	DO (mg/L)	Sp Cond (uS/cm)	pH	ORP (mV)	Purged Volume (gal)	Water Level
11:19	11.36	1.4	1906	6.13	27	2.5	7.33
11:22	11.34	1.87	1832	6.2	19	4.5	7.33
11:25	11.35	2.01	1829	6.22	7	6.5	7.33
11:28	11.34	2.1	1820	6.23	1	8	7.33
11:31	11.47	2.46	1809	6.23	-3	9.5	Stable
11:34	11.45	2.76	1805	6.24	-7	11.5	Stable
11:37	11.34	2.92	1790	6.25	-11	13	Stable
11:39	11.34	3.03	1783	6.25	-14	14.2	Stable
11:42	11.3	3.07	1782	6.25	-17	16	Stable
11:45	11.34	3.11	1793	6.26	-20	17.3	Stable

Note. Well diameter is 12", well depth is 11.6", bladder pump was used at a depth of 9' and a rate of 4 L/min; static water level was 7.33'. Purge water was light brown with a slight sulfur odor.
DO = dissolved oxygen; ORP = oxidation/redox potential; Sp Cond = specific conductance.

Table A-6. Results of screening water samples collected on March 9, 2022.

Analyte	Analyte Group	DW-3	Qualifier	DW-3 REP	Qualifier	Units	Method
Antimony	metals	1.3	—	1.26	—	ug/L	EPA200.8
Arsenic	metals	0.37	—	0.37	—	ug/L	EPA200.8
Beryllium	metals	0.1	U	0.1	U	ug/L	EPA200.8
Cadmium	metals	0.02	U	0.02	U	ug/L	EPA200.8
Chromium	metals	0.33	—	0.34	—	ug/L	EPA200.8
Copper	metals	1.84	—	1.82	—	ug/L	EPA200.8
Lead	metals	0.163	—	0.167	—	ug/L	EPA200.8
Nickel	metals	0.3	—	0.31	—	ug/L	EPA200.8
Selenium	metals	0.18	—	0.18	—	ug/L	EPA200.8
Silver	metals	0.02	U	0.02	U	ug/L	EPA200.8
Thallium	metals	0.1	U	0.1	U	ug/L	EPA200.8
Zinc	metals	1	U	1	U	ug/L	EPA200.8
Hardness as CaCO3	metals	260	—	261	—	mg/L	SM2340B
Potassium	Anions/Cations	4.21	—	4.28	—	mg/L	EPA200.7
Magnesium	Anions/Cations	9.54	—	9.58	—	mg/L	EPA200.7
Sodium	Anions/Cations	156	—	157	—	mg/L	EPA200.7
Calcium	Anions/Cations	88.3	—	88.9	—	mg/L	EPA200.7
Bromide	Anions/Cations	0.032	—	0.031	—	mg/L	EPA300.0
Chloride	Anions/Cations	413	—	408	—	mg/L	EPA300.0
Fluoride	Anions/Cations	0.1	U	0.1	U	mg/L	EPA300.0
Sulfate	Anions/Cations	6.92	—	6.91	—	mg/L	EPA300.0
Ammonia	Anions/Cations	0.01	U	0.01	U	mg/L	SM4500NH3H
Nitrate-Nitrite as N	Anions/Cations	1.21	—	1.21	—	mg/L	SM4500NO3I
Dissolved Organic Carbon	Anions/Cations	1.77	—	2.02	—	mg/L	SM5310B
Gasoline	Organics	0.07	U	0.07	U	mg/L	NWTPH-GX
Benzene	Organics	1	U	1	U	ug/L	SW8021B
Ethylbenzene	Organics	1	U	1	U	ug/L	SW8021B
Toluene	Organics	1	U	1	U	ug/L	SW8021B
m,p-Xylene	Organics	2	U	2	U	ug/L	SW8021B
o-Xylene	Organics	1	U	1	U	ug/L	SW8021B
1-Methylnaphthalene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM

Analyte	Analyte Group	DW-3	Qualifier	DW-3 REP	Qualifier	Units	Method
2-Chloronaphthalene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
2-Methylnaphthalene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
Acenaphthene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
Acenaphthylene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
Anthracene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
Benz[a]anthracene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
Benzo(a)pyrene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
Benzo(b)fluoranthene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
Benzo(ghi)perylene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
Benzo(k)fluoranthene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
Carbazole	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
Chrysene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
Dibenzo(a,h)anthracene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
Dibenzofuran	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
Fluoranthene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
Fluorene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
Indeno(1,2,3-cd)pyrene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
Naphthalene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
Phenanthrene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
Pyrene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM
Retene	Organics	0.0493	U	0.0493	U	ug/L	SW8270ESIM

U = analyte not detected above the PQL.

Table A-7. Field parameters measured during well purging on February 1, 2023.

Time	Temp (deg C)	DO (mg/L)	Sp Cond (uS/cm)	pH	ORP (mV)	Purged Volume (gal)	Water Level
10:04	11.01	1.59	1203	6.04	68	1.5	6.8
10:08	11.2	1.94	1197	6.17	49	5	6.8
10:12	11.25	1.84	1206	6.21	33	8.8	6.8
10:16	11.26	1.66	1220	6.23	25	12.3	6.8
10:20	11.29	1.38	1225	6.24	19	16	Stable
10:24	11.29	1.19	1237	6.24	14	19.8	Stable
10:28	11.32	0.95	1241	6.24	11	23.5	Stable
10:32	11.33	0.74	1253	6.24	7	31.2	Stable
10:36	11.36	0.68	1241	6.25	5	35	Stable
10:40	11.35	0.76	1241	6.24	3	39	Stable
10:44	11.35	0.79	1250	6.24	2	43	Stable
10:48	11.34	0.75	1243	6.24	1	46	Stable

Note. Well diameter is 12", well depth is 11.6", bladder pump was used at a depth of 9' and a rate of 3.75 L/min; static water level was 7.33'. Purge water was light brown to yellow with a slight sulfur odor.

DO = dissolved oxygen; ORP = oxidation/redox potential; Sp Cond = specific conductance.
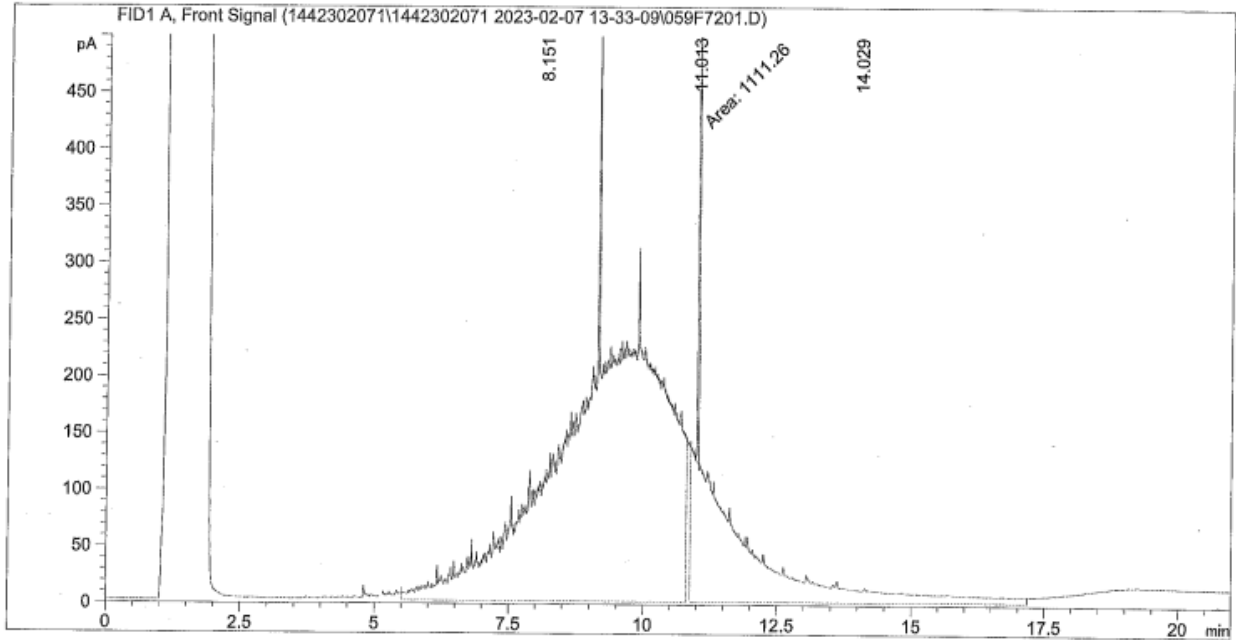
Figure A-1. Chromatogram from Lab 1 of the diesel range organics unresolved complex mixture at the study sample site.
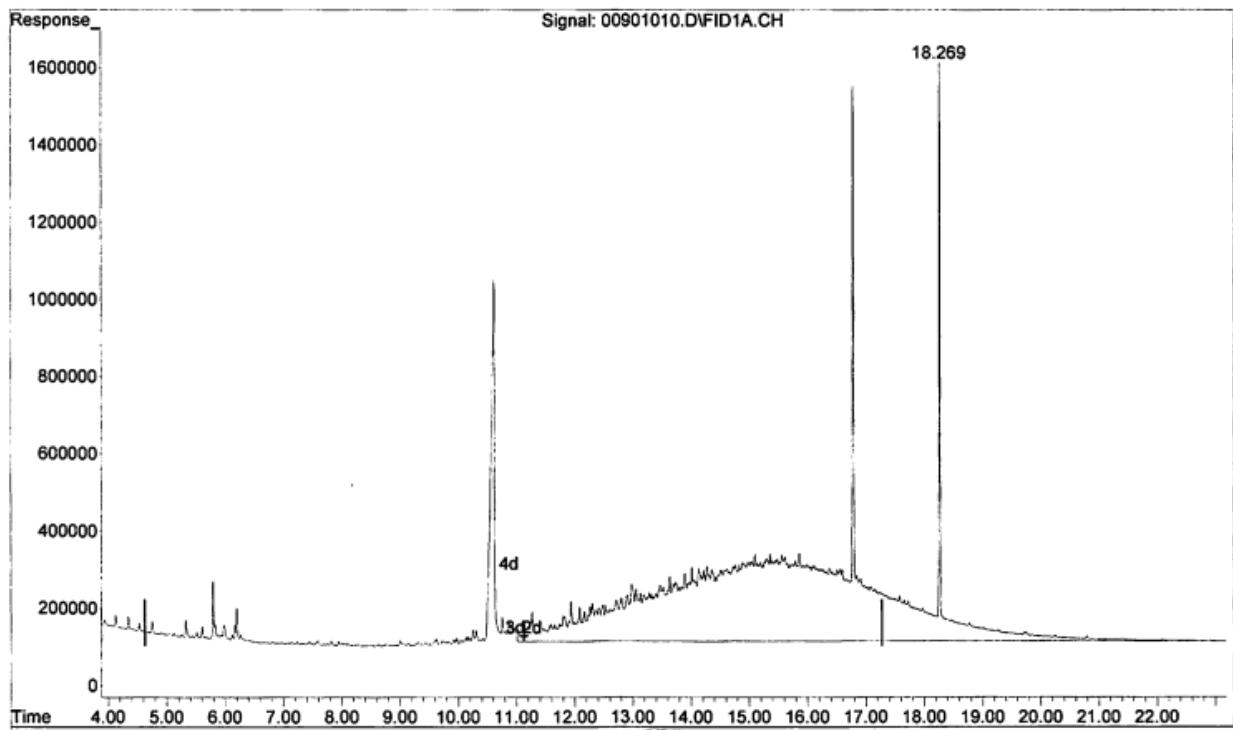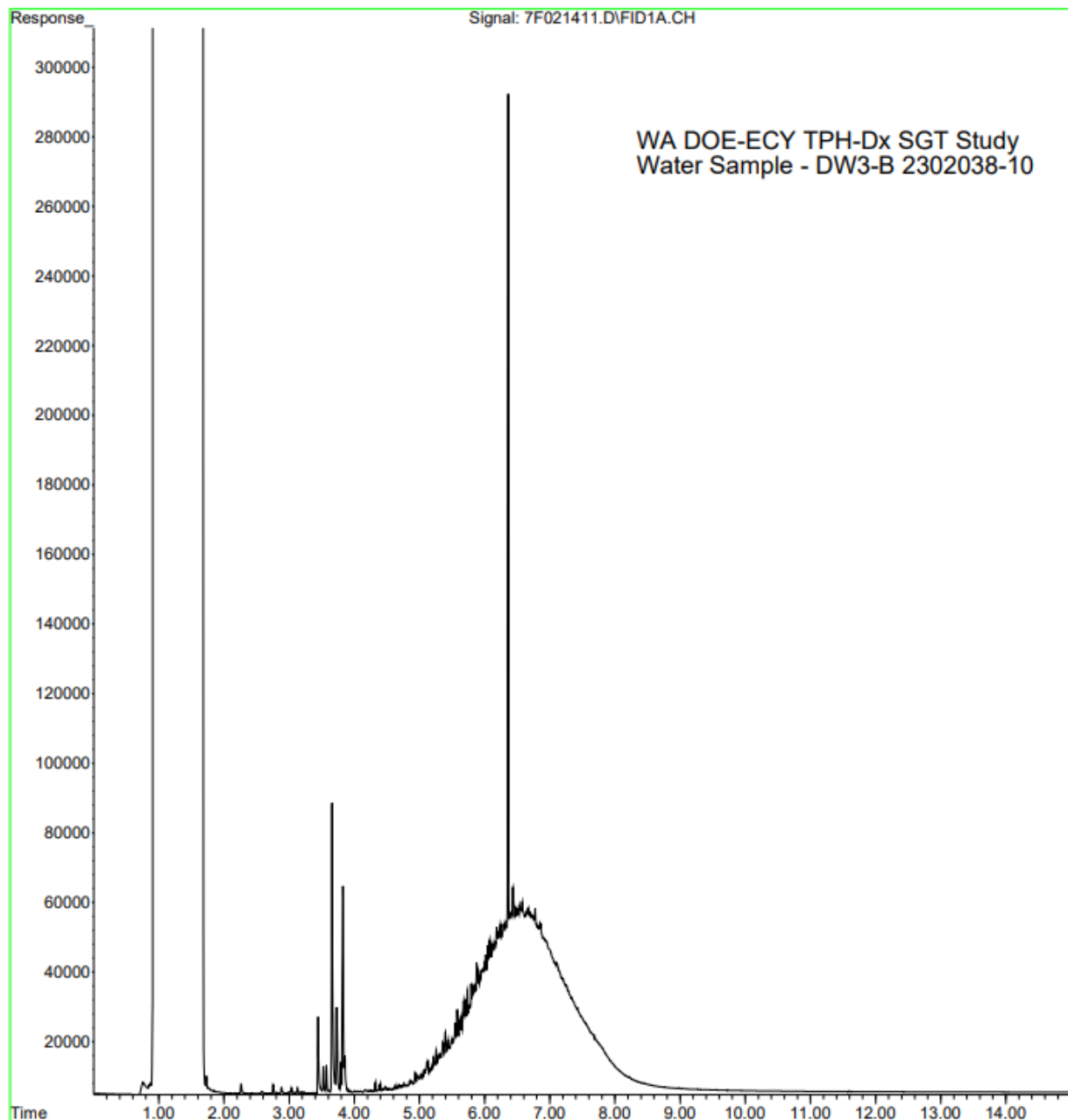

Figure A-2. Chromatogram from Lab 2 of the diesel range organics unresolved complex mixture at the study sample site.

Figure A-3. Chromatogram from Lab 3 of the diesel range organics unresolved complex mixture at the study sample site.
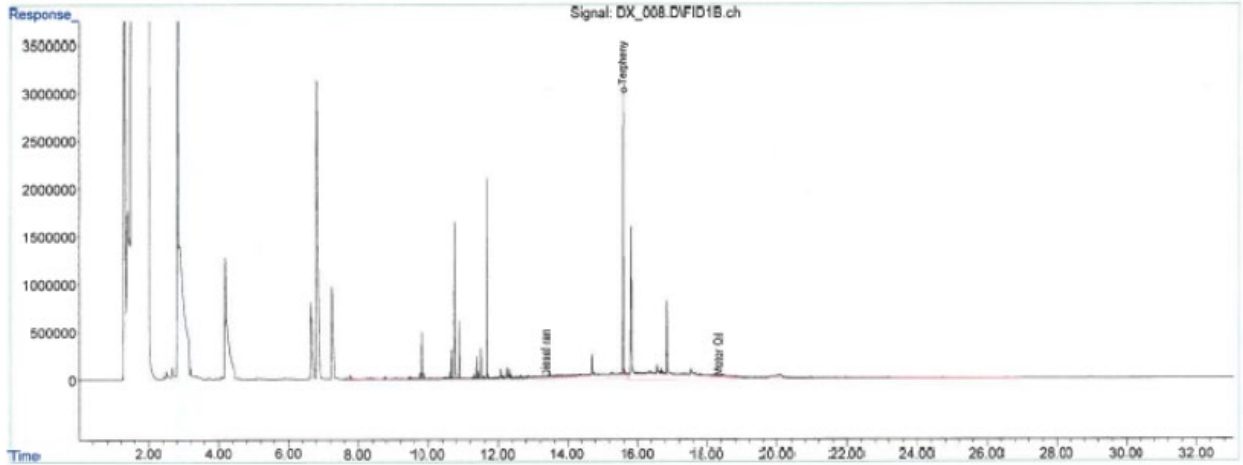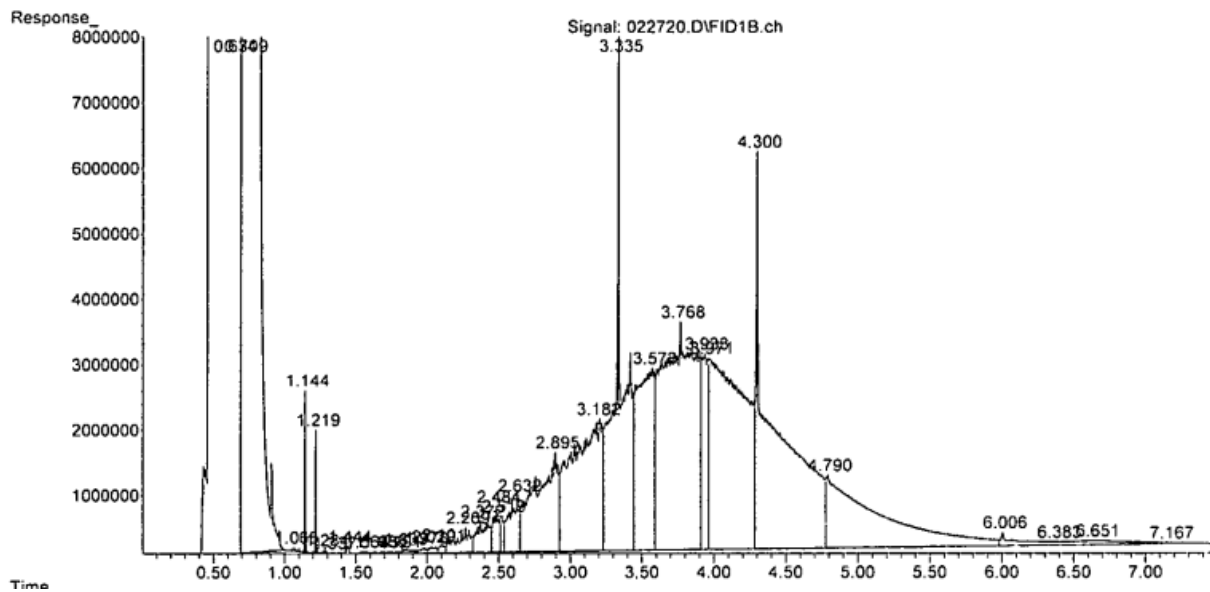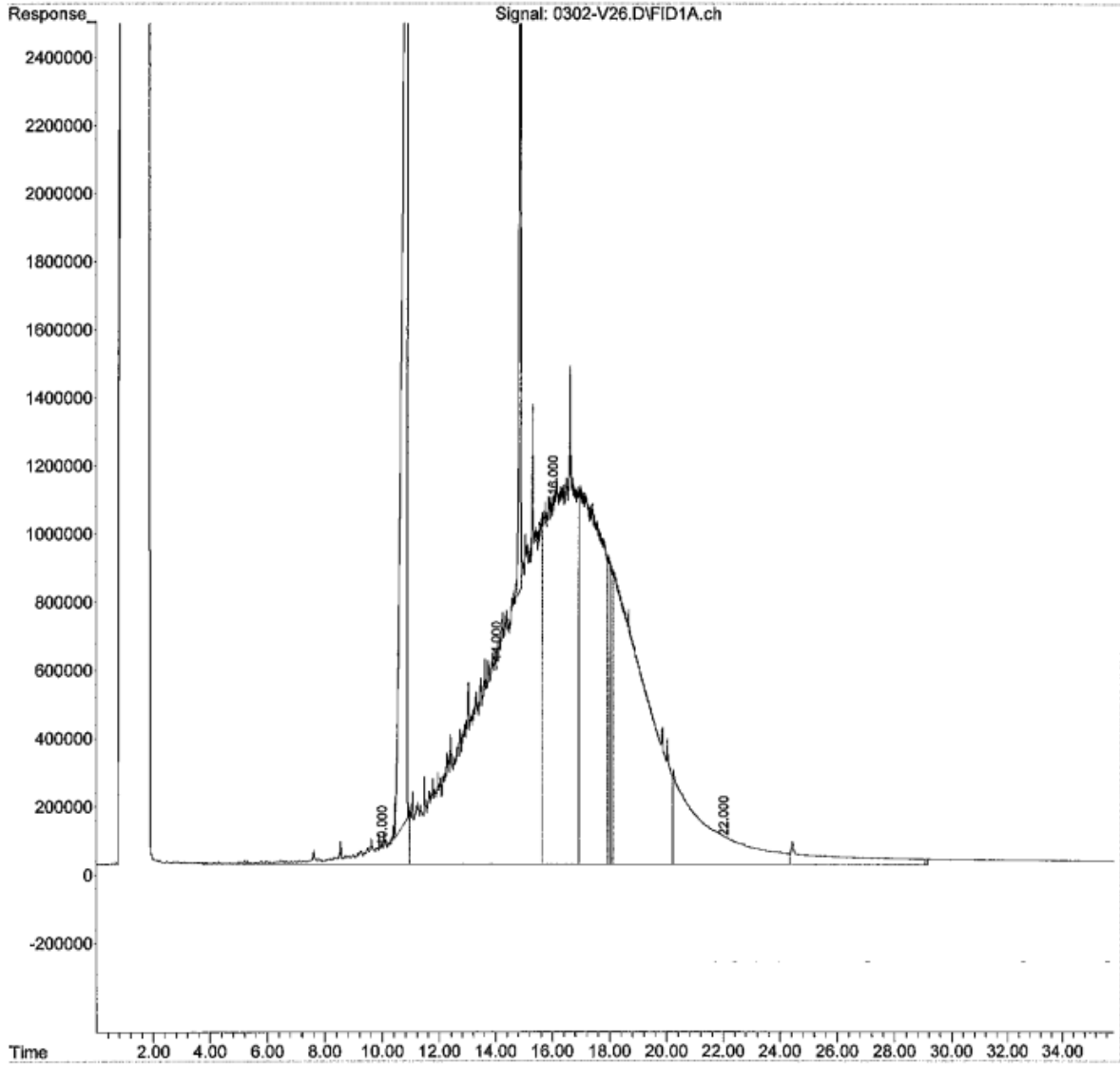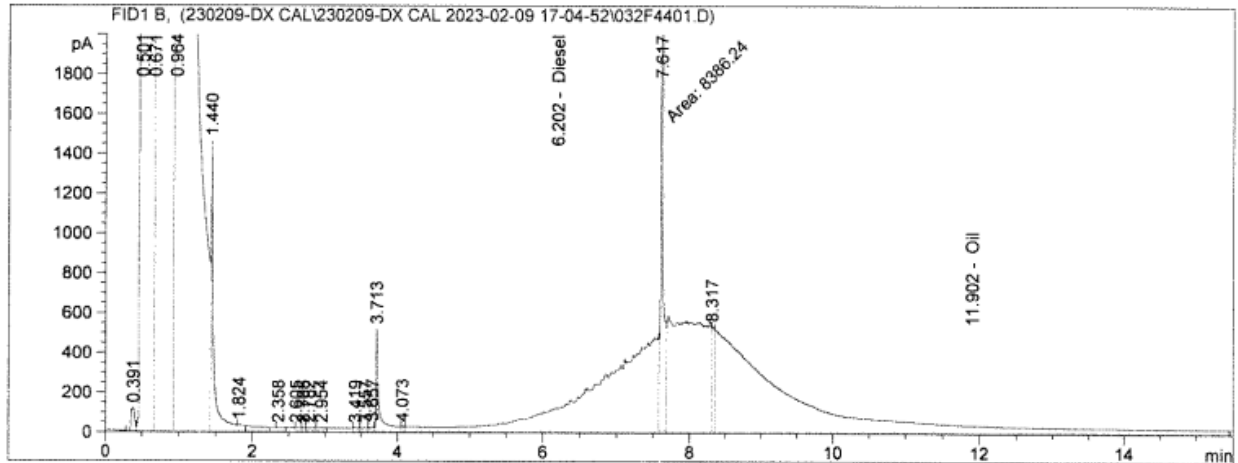
Figure A-4. Chromatogram from Lab 4 of the diesel range organics unresolved complex mixture at the study sample site.

Figure A-5. Chromatogram from Lab 5 of the diesel range organics unresolved complex mixture at the study sample site.

Figure A-6. Chromatogram from Lab 6 of the diesel range organics unresolved complex mixture at the study sample site.

Figure A-7. Chromatogram from Lab 7 of the diesel range organics unresolved complex mixture at the study sample site.
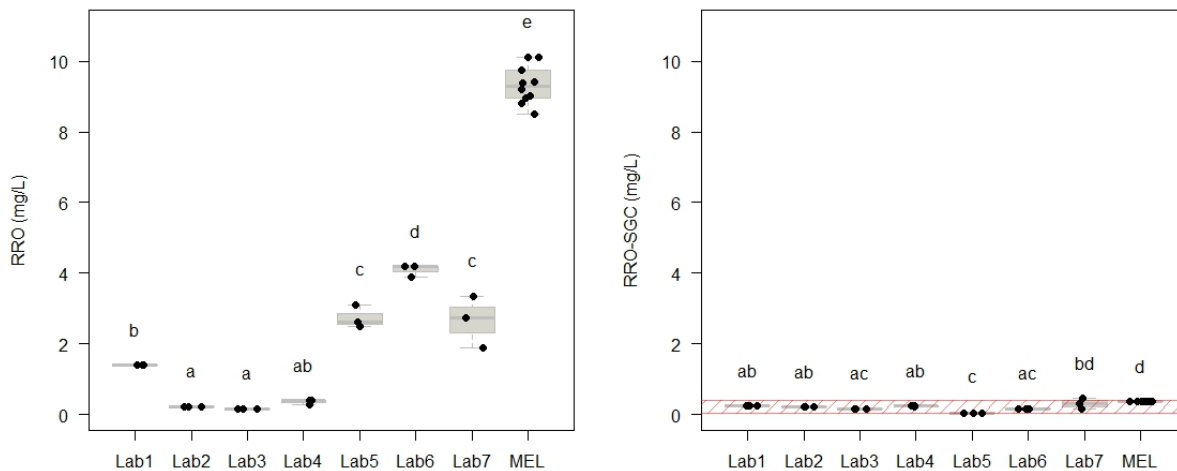
Figure A-8. Box and Whiskers plots of uncleaned (RRO) and cleaned (RRO-SGC) samples.

The red shaded area on the right plot delineates the range of PQL values among the labs. Letters above the boxes signify statistical significance at the level of $\alpha = 0.05$, in accordance with the ANOVA and post-hoc tests.

Appendix B. Analytical QC Tables

Appendix B is linked to this report at
https://apps.ecology.wa.gov/publications/SummaryPages/2403001.html

Appendix C. Data Validation Report

Appendix C is linked to this report at:
https://apps.ecology.wa.gov/publications/SummaryPages/2403001.html