DEPARTMENT OF
ECOLOGY
State of Washington

Quality Assurance Project Plan

Guidance for the WDOE NWTPH-Dx Method for Testing Groundwater

January 2022

Publication 22-03-101

Publication Information

Each study conducted by the Washington State Department of Ecology must have an approved Quality Assurance Project Plan (QAPP). The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completing the study, Ecology will post the final report of the study to the Internet.

The final QAPP is available on Ecology's website at https://apps.ecology.wa.gov/publications/SummaryPages/2203101.html.

Suggested Citation
Hobbs, WO. 2022. Quality Assurance Project Plan: Guidance for the WDOE NWTPH-Dx Method for Testing Groundwater. Publication 22-03-101. Washington State Department of Ecology, Olympia. https://apps.ecology.wa.gov/publications/SummaryPages/2203101.html.

The Activity Tracker Code for this study is 21-014.

Federal Clean Water Act 1996 303(d) Listings Addressed in this Study. See Section 3.3.

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, Bellevue	425-649-7000
Southwest Regional Office, Olympia	360-407-6300
Central Regional Office, Union Gap	509-575-2490
Eastern Regional Office, Spokane	509-329-3400

Quality Assurance Project Plan

Guidance for the WDOE NWTPH-Dx Method for Testing Groundwater

by William Hobbs

January 2022

Approved by:

Signature:	Date:
Arthur Buchan, Client, Toxics Cleanup Program	
Signature:	Date:
Richelle Perez, Client's Unit Supervisor, Toxics Cleanup Program	
Signature:	Date:
Jeff Johnston, Client's Section Manager, Toxics Cleanup Program	
Signature:	Date:
William Hobbs, Author / Project Manager, EAP	
Signature:	Date:
James Medlen, Author's Unit Supervisor, EAP	
Signature:	Date:
Jessica Archer, Author's Section Manager, EAP	
Signature:	Date:
Joan Protasio, Interim Organics Unit Supervisor/Project Investigator, Manchester Environmental Laboratory, EAP	
Signature:	Date:
Alan Rue, Director, Manchester Environmental Laboratory, EAP	
Signature:	Date:
Arati Kaza, Ecology Quality Assurance Officer	

Signatures are not available on the Internet version.
EAP: Environmental Assessment Program

1.0 Table of Contents

Page

List of Figures

List of Tables

2.0 Abstract

Under the Model Toxics Control Act (MTCA) Cleanup Regulation, Method A is one of the most common approaches used to establish cleanup levels that are applicable to groundwater impacted by hydrocarbons. Under Method A of the regulation, a total petroleum hydrocarbon (TPH) approach may be taken. In 1997, the Washington State Department of Ecology (Ecology) published analytical methods for TPH. These include methods for:

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

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.

The SGC step in the NWTPH-Dx method calls for silica gel to be added as free-flowing in a "shake" method. However, a silica gel column method has been shown to have a higher removal efficiency of the polar compounds that can interfere with the DRO result. Furthermore, the use of sulfuric acid prior to the SGC is recommended in the method; however, it is unlikely that regional labs follow this step.

This project will survey accredited labs to ascertain how the NWTPH-Dx method is currently being used. Participating labs will then work with Ecology's Manchester Environmental Laboratory to (1) provide guidance on how the SGC step within the NWTPH-Dx method could be improved and clarified for groundwater samples and (2) participate in an interlaboratory comparison using a revised approach.

3.0 Background

3.1 Introduction and problem statement

In 1997, the Washington State Department of Ecology (Ecology) published analytical methods for petroleum hydrocarbons (Ecology, 1997). These methods related directly 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 used to establish cleanup levels that are applicable to groundwater impacted by hydrocarbons. Under Method A of the regulation, a total petroleum hydrocarbon (TPH) approach may be taken. The approach to evaluate TPH includes two methods:

- NWTPH-Gx – gasoline range organics (GRO)
- NWTPH-Dx – diesel range organics (DRO)[1].

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 method can also capture petroleum degradates, or metabolites that are non-hydrocarbon polar compounds.

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 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 prior to analysis on the gas chromatograph.

The current guidance on the use of SGC on groundwater samples for contaminated site investigations and cleanup is that NWTPH-Dx concentrations must be measured with and without SGC for it 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 there have been no updates or guidance 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 (USEPA, 1996), has been shown to have a higher removal efficiency of polar compounds (Zemo et al., 2013). In addition, the SGC step calls for the use of sulfuric acid prior to the addition of silica gel, which can remove some of the heavier sulfur containing hydrocarbons. Currently, this step is not routinely carried out on groundwater samples by Ecology's Manchester Environmental Laboratory (MEL) unless specifically requested. It is unknown whether other regional labs routinely use the complete NWTPH-Dx method on groundwater or a modified version.

---

[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.

There are about 35 laboratories accredited by Ecology for the NWTPH-Dx method in non-potable waters. This project will survey accredited labs to ascertain how the NWTPH-Dx method is currently being used. Participating labs will then work with MEL to develop guidance on how the SGC step within the NWTPH-Dx method could be improved and clarified for groundwater samples. This project will not provide guidance on *when* the SGC step should be used on groundwater samples during site investigations.

3.2 Study area and surroundings

This project is relevant to TCP petroleum cleanup sites throughout Washington State.

3.2.1 History of study area

Not applicable

3.2.2 Summary of previous studies and existing data

Ecology's previous work on establishing environmental effects thresholds for weathered DRO on aquatic organisms gives an example of the change in concentrations during the SGC steps (Figure 1). The SGC steps included in the earlier work followed the NWTPH-Dx method: free-flowing silica gel and the additional sulfuric acid step. Using the "shake" or free-flowing method for adding silica gel to the extract reduced the DRO concentrations considerably. When the sulfuric acid cleanup step was used prior to the silica gel being added the concentrations were reduced to at or near the practical quantitation limit (0.25 mg/L in this study). Similar reductions in the concentrations of RRO were observed following SGC (Hobbs et al., 2020).

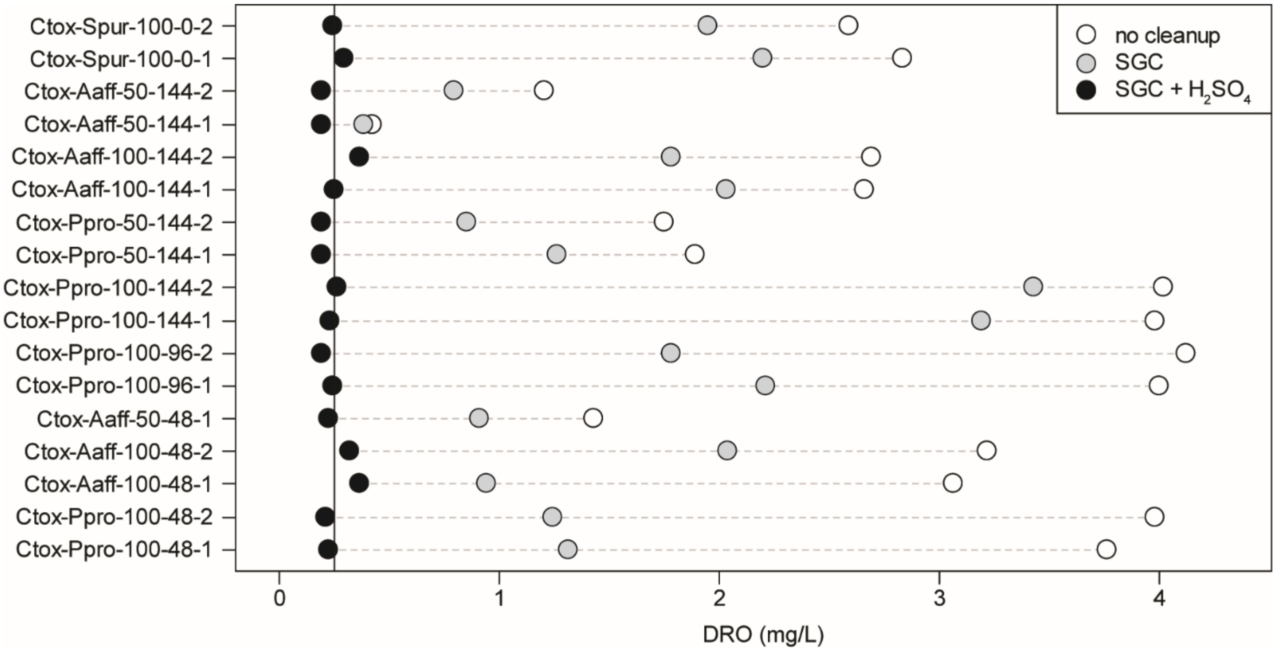


Figure 1: DRO concentrations of replicate samples with no cleanup and silica gel cleanup (SGC) (Hobbs et al., 2020).

SGC with H_2SO_4 includes the additional sulfuric acid cleanup as per the NWTPH-Dx method. Vertical line represents the 0.25 mg/L cleanup standard (WAC-173-340-730).

The chromatogram of the weathered DRO from the previous study is shown in Figure 2. The composition of the DRO is what would be referred to as an "unresolved complex mixture", where no distinct petroleum peaks are observed (Gough and Rowland 1990). Our goal is to use the same sample location and weathered diesel composition for the current project.

3.2.3 Parameters of interest and potential sources

This study is focused on diesel range organics (DROs) as defined by the NWTPH-Dx method. DRO includes petroleum hydrocarbons in the C12-C24 range and heavy oil-range petroleum hydrocarbons. Diesel-contaminated groundwater becomes weathered through microbial degradation, sorption to soils, and dissolution (Lang et al. 2009). Weathering of diesel-contaminated surface waters can also occur through photooxidation and volatilization. Degradation products derived from weathering of the hydrocarbons and can be referred to as polar compounds, petroleum metabolites, or degradates.

The ability to identify petroleum metabolites using gas chromatography has improved over time (O'Reilly et al., 2019; Mohler et al., 2020). Generally, as the petroleum products oxidize and carbon chains are broken and transformed, there is a shift towards heavier compounds and longer elution times during analysis (Figure 3). These oxygen-containing organic compounds (OCOCs) can be screened into five main functional groups: alcohols, ketones, phenols, aldehydes, and esters (Mohler et al., 2020). Guidance by Ecology's Toxics Cleanup Program (TCP) states that petroleum metabolites should be considered part of the NWTPH-Dx result for the purposes of site characterization and compliance (Ecology, 2016). The use of silica gel cleanup as an analytical preparation method to remove polar petroleum metabolites is permitted only when the groundwater is naturally high in organic matter that would interfere with the quantification of DROs.

3.2.4 Regulatory criteria or standards

TCP has guidance on the remediation of petroleum-contaminated sites (Ecology, 2016). Part of remediating a contaminated site is establishing a level or concentration of petroleum hydrocarbons as a "cleanup standard". For waters of the state, WAC 173-340-730 (3)(b)(iii)(C) states that Method A groundwater TPH cleanup levels may be used as surface water Method B petroleum cleanup levels protective of human health. The cleanup level for diesel range organics by NWTPH-Dx under Method A is 500 µg/L.

Site-specific protective concentrations can be derived using Method B Equations 730-1 and 730-2 (WAC 173-340-730 pg. 164). However, the concentration calculated under Method B would then default to the practical quantitation limits (PQLs) for NWTPH-Dx of 500 µg/L, if the calculated protective value is lower than the PQL for the specific contaminant.

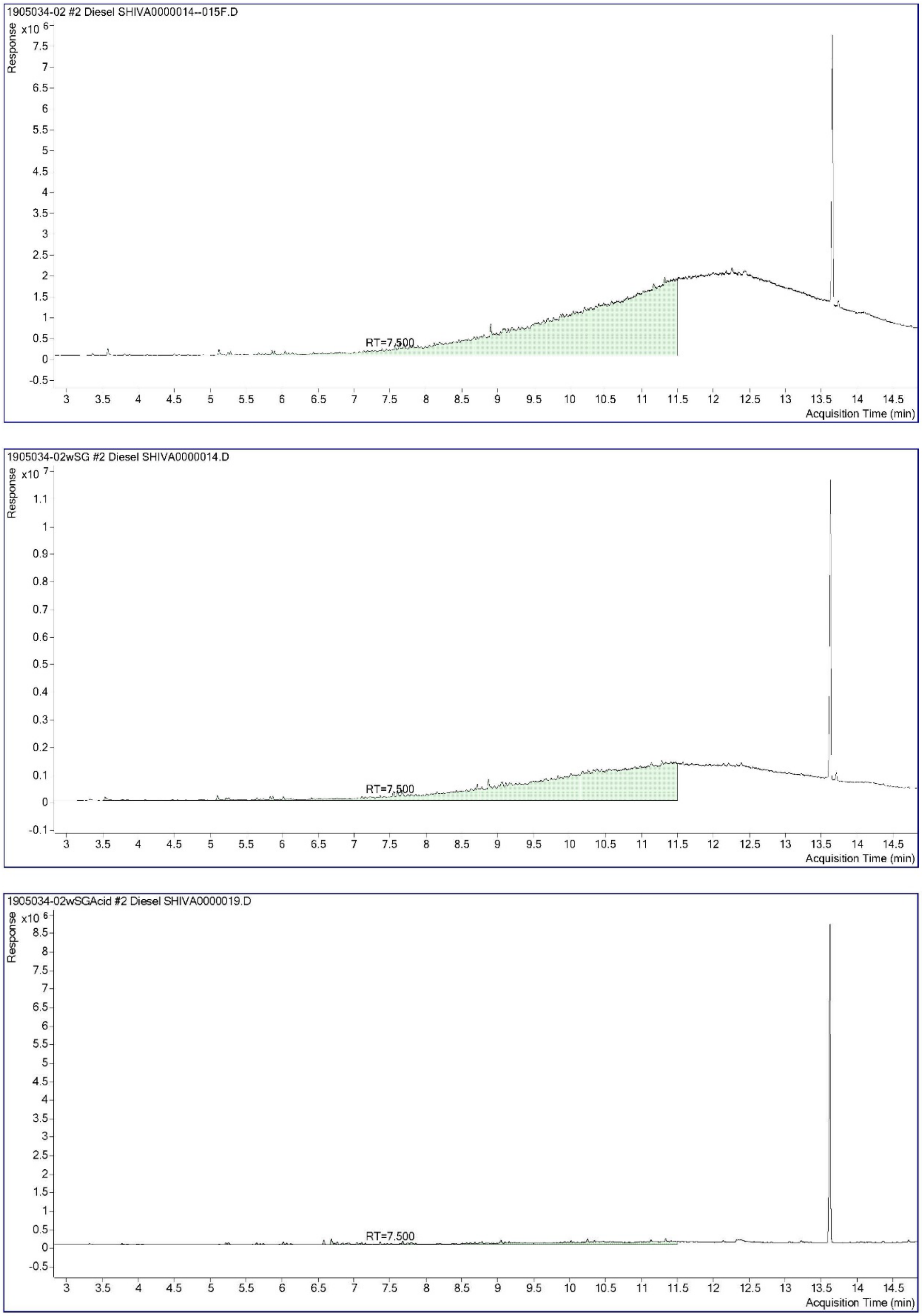


Figure 2: Chromatograms from the diesel-range organics (DRO) in samples from Hobbs et al. (2020). *Chromatograms represent raw sample (upper), free-flowing silica cleanup (middle), and SGC and sulfuric acid cleanup (lower). Shaded regions of the curve represent the area quantified for reported concentrations (mg/L).*

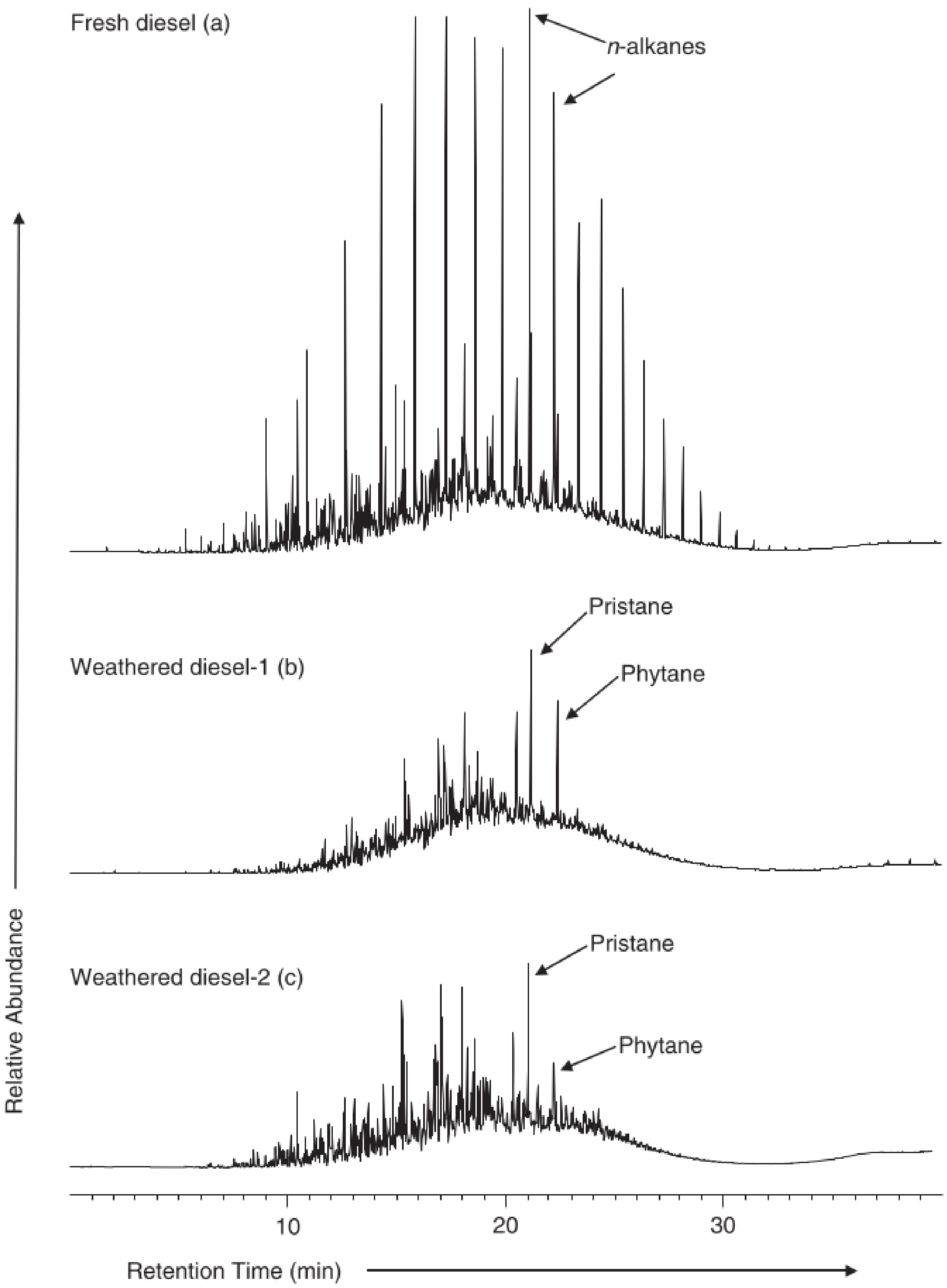


Figure 3. Gas chromatograph of fresh (a) and weathered (b and c) diesel fuel (Lang et al., 2009).

The highlighted compound peaks on the chromatograms describe the degradation of n-alkanes relative to the resistant compounds of pristane and phytane.

4.0 Project Description

Since the publication of the NWTPH-Dx method by Ecology in 1997, the application of the silica gel cleanup to samples of DRO in groundwater has been inconsistent. Work since the original publication and Ecology's anecdotal understanding of the variability in how regional laboratories are using the SGC steps, has led to the current project.

4.1 Project goals

The project goal is to provide guidance on how laboratories should be using silica gel cleanup (SGC) on groundwater samples contaminated with weathered diesel range organics.

4.2 Project objectives

The project objectives include:

- Conduct a survey of regional laboratories accredited for NWTPH-Dx and their SGC methods.
- Validate a SGC method based on a combination of Zemo et al. (2013) and EPA 3630C for NWTPH-Dx.
- Conduct an interlaboratory comparison of MEL's validated SGC method used with the NWTPH-Dx analytical method for water samples.
- Provide recommendations on the SGC protocol that are compatible with Washington's NWTPH-Dx method, WAC 173-340 and current knowledge with input from regional laboratories.

4.3 Information needed and sources

As part of the initial stages of this project, Ecology distributed a survey to regional (Washington, Idaho and Oregon) contract labs that are accredited for the WDOE[2] NWTPH-Dx method in non-potable water. The survey can be found in Appendix A. The goal of this initial information gathering exercise is to evaluate the possible variability in the protocol and application of silca gel methods among the labs. Furthermore, labs were asked to describe whether and how they feel the method should be revised.

4.4 Tasks required

The project tasks include:

- Write and receive quality assurance approval for the study QAPP.
- Survey regional laboratories to evaluate the variability in internal cleanup procedures; also evaluate lab willingness to provide review and participate in method revision.
- MEL writes a modified method or lab SOP describing the recommended SGC protocol based on Ecology (1997), EPA 3630C/3665A, and Zemo et al. (2013). MEL asks accredited labs to review the method

---

[2] WDOE – Washington State Department of Ecology

- Recover about 150 L of groundwater contaminated with weathered diesel from the site used in previous NWTPH-Dx toxicity study (Hobbs et al., 2020).
- Manchester Environmental Laboratory (MEL) characterizes the groundwater chemistry (e.g. TPH, cations, anions, nutrients and metals). The bulk collections are stored at the Environmental Assessment Program (EAP) Operations Center, Chain-of-Custody Room, for further testing.
- Sample aliquots of the bulk collection are shipped to contract labs for an interlaboratory comparison study. The interlaboratory study conforms with ASTM E691-19 (2019).
- An EAP report is the final product. Recommendations will be used by TCP's Policy and Technical Support Section to write guidance documents and possibly amend the methods document (Ecology, 1997).

4.5 Systematic planning process

This QAPP represents the systematic planning process.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 1 shows the responsibilities of those who will be involved in this project.

Table 1. Organization of project staff and responsibilities.

Staff[1]	Title	Responsibilities
Arthur Buchan TCP Phone: 360-407-7146	EAP Client	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.
William Hobbs TSU-SCS-EAP Phone: 360-407-7512	Project Manager	Writes the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data, and enters data into EIM. Writes the draft report and final report.
Joan Protasio MEL-EAP Phone: 360-871-8820	Project Scientist	Supervises laboratory analysis of samples; writes revised method protocol for NWTPH-Dx in groundwater using silica gel cleanup.
Christina Frans MEL-EAP Phone: 360-871-8829	QA Coordinator, Manchester Lab	Drafts contract laboratory scope of work; Conducts QA review of contract laboratory data.
James Medlen TSU-SCS-EAP Phone: 360-407-6775	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Jessica Archer SCS-EAP Phone: 360-407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Alan Rue MEL-EAP Phone: 360-871-8801	Manchester Lab Director	Reviews and approves the final QAPP.
Arati Kaza Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP.

TCP: Toxics Cleanup Program; TSU: Toxics Studies Unit; SCS: Statewide Coordination Section; EAP: Environmental Assessment Program; QAPP: Quality Assurance Project Plan; MEL: Manchester Environmental Laboratory.

5.2 Special training and certifications

Not applicable

5.3 Organization chart

See Table 1.

5.4 Proposed project schedule

Tables 2 and 3 list key activities, due dates, and lead staff for this project.

Table 2. Schedule for completing field and laboratory work

Task	Due date	Lead staff
Draft QAPP	September 2021	Hobbs
Final QAPP	January 2022	Hobbs
Field Work	January 2022	Hobbs
Laboratory analyses	May 2022	Protasio/Chuhran
Contract lab data validation	June 2022	Frans

Table 3. Schedule for final report

Task	Due date	Lead staff
Draft to supervisor	September 2022	Hobbs
Draft to client/ peer reviewer	October 2022	Hobbs
Draft to external reviewers	November 2022	Hobbs
Final draft to publications team	December 2022	Hobbs
Final report due on web	March 2023	Hobbs

5.5 Budget and funding

Funding for this project is through funds, administered by TCP, from the Washington State Toxics Control Account.

Table 4. Project budget and funding

Item	Cost ($)	Subtotals
Laboratory – MEL (incl. contracting)	$13,025	$33,810
Laboratory – contract lab	$15,150	
Laboratory – *contingency (20%)	$5,635	
Equipment/shipping	$2,500	$2,500
Personnel (TSU senior scientist and MEL chemist)	$66,239	$66,239
		$102,549

MEL: Manchester Environmental Laboratory
TSU: EAP's Toxics Studies Unit

Table 5. Laboratory budget details

Parameter	Number of Samples	Number of QA Samples	Total Number of Samples	Cost Per Sample ($)	Lab Subtotal ($)
Screening: general chemistry and hydrocarbons	1	1	2	$1015	$2,030
Method development: NWTPH-Dx	30	0	30	$160	$4,800
Interlab (MEL): NWTPH-Dx	15	0	15	$160	$2,400
Interlab (Contract): NWTPH-Dx	90	0	90	$160	$14,400

6.0 Quality Objectives

6.1 Data quality objectives

The data quality objectives (DQOs) for the analytical portion of the study are described below in the Measurement Quality Objectives section. Following MEL's sample collection and characterization of the groundwater chemistry, a small interlaboratory comparison study will be carried out using a revised SGC protocol. This interlab study will conform to the ASTM standard, "*Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method (E691-19).*" Under this standard, a minimum of 8 labs need to participate; our goal is to have 15 labs participating. Each lab will receive triplicate samples of the study groundwater for analysis of DRO and DRO with SGC on the same extract; this level of replication complies with the ASTM standard. The results from the contract labs will be statistically evaluated for precision and compared with the results from MEL.

6.2 Measurement quality objectives

6.2.1 Targets for precision, bias, and sensitivity

The measurement quality objectives (MQOs) for project results, expressed in terms of acceptable precision, bias, and sensitivity, are described in this section and summarized in Table 6.

Table 6. Measurement quality objectives for water chemistry.

Parameter	Precision		Bias			Sensitivity
	Field duplicate samples	Matrix spike-duplicates	Verification standards (LCS)	Matrix spikes	Surrogate standards*	Reporting limit
	Relative percent difference (RPD)		Recovery limits (%)			Concentration units
Organics						
NWTPH-Dx (DRO)†	<40%	<40%	70-130%	70-130%	50-150%	0.15 mg/L
NWTPH-Gx (GRO)‡	<50%	<40%	70-130%	70-130%	70-130%	0.07 mg/L
Volatile petroleum hydrocarbons (VPH)	<30%	<30%	70-130%	70-130%	70-130%	50 µg/L
Extractable petroleum hydrocarbons (EPH)	<30%	<30%	70-130%	70-130%	70-130%	40 µg/L
Benzene	<50%	<50%	70-130%	70-130%	70-130%	1.0 µg/L
Ethylbenzene	<50%	<50%	70-130%	70-130%	70-130%	1.0 µg/L
Toluene	<50%	<50%	70-130%	70-130%	70-130%	1.0 µg/L
Xylenes	<50%	<50%	70-130%	70-130%	70-130%	2.0 µg/L
Polynuclear aromatic hydrocarbons (PAHs)						
1-Methylnaphthalene	<50%	<40%	41-117%	39-113%	NA	0.05 µg/L
2-Chloronaphthalene	<50%	<40%	50-150%	50-150%	NA	0.05 µg/L

Parameter	Precision		Bias			Sensitivity
	Field duplicate samples	Matrix spike-duplicates	Verification standards (LCS)	Matrix spikes	Surrogate standards*	Reporting limit
	Relative percent difference (RPD)		Recovery limits (%)			Concentration units
2-Methylnaphthalene	<50%	<40%	36-112%	34-105%	NA	0.05 µg/L
Acenaphthene	<50%	<40%	40-112%	55-97%	NA	0.05 µg/L
Acenaphthylene	<50%	<40%	10-126%	48-103%	11-139%	0.05 µg/L
Anthracene	<50%	<40%	24-127%	51-113%	27-132%	0.05 µg/L
Benzo(a)anthracene	<50%	<40%	38-147%	59-137%	NA	0.05 µg/L
Benzo(a)pyrene	<50%	<40%	14-129%	42-110%	29-120%	0.05 µg/L
Benzo(b)fluoranthene	<50%	<40%	42-133%	53-99%	NA	0.05 µg/L
Benzo(g,h,i)perylene	<50%	<40%	12-122%	38-131%	NA	0.05 µg/L
Benzo(k)fluoranthene	<50%	<40%	38-131%	33-122%	NA	0.05 µg/L
Carbazole	<50%	<40%	42-133%	63-123%	NA	0.05 µg/L
Chrysene	<50%	<40%	37-128%	51-116%	NA	0.05 µg/L
Dibenzo(a,h)anthracene	<50%	<40%	10-134%	27-129%	NA	0.05 µg/L
Dibenzofuran	<50%	<40%	39-121%	47-105%	NA	0.05 µg/L
Fluoranthene	<50%	<40%	42-123%	60-107%	NA	0.05 µg/L
Fluorene	<50%	<40%	50-150%	50-150%	43-112%	0.05 µg/L
Indeno(1,2,3-cd)pyrene	<50%	<40%	29-129%	37-135%	NA	0.05 µg/L
Naphthalene	<50%	<40%	41-105%	41-97%	NA	0.05 µg/L
Phenanthrene	<50%	<40%	18-105%	18-105%	NA	0.05 µg/L
Pyrene	<50%	<40%	43-131%	61-118%	48-143%	0.05 µg/L
Retene	<50%	<40%	10-151%	57-139%	NA	0.05 µg/L
Inorganics						
Major ions						
Sodium	<20%	<20%	85-115%	75-125%	NA	0.025 mg/L
Magnesium	<20%	<20%	85-115%	75-125%	NA	0.025 mg/L
Potassium	<20%	<20%	85-115%	75-125%	NA	0.25 mg/L
Calcium	<20%	<20%	85-115%	75-125%	NA	0.025 mg/L
Sulfate	<20%	<20%	90-110%	75-125%	NA	0.30 mg/L
Chloride	<20%	<20%	90-110%	75-125%	NA	0.10 mg/L
Bromide	<20%	<20%	90-110%	75-125%	NA	0.10 mg/L
Fluoride	<20%	<20%	90-110%	75-125%	NA	0.10 mg/L

Parameter	Precision		Bias			Sensitivity
	Field duplicate samples	Matrix spike-duplicates	Verification standards (LCS)	Matrix spikes	Surrogate standards*	Reporting limit
	Relative percent difference (RPD)		Recovery limits (%)			Concentration units
Sulfides	<20%	<20%	75-125%	75-120%	NA	0.05 mg/L
Nutrients						
Ammonia	<20%	<20%	80-120%	75-125%	NA	0.01 mg/L
Nitrate-nitrite	<20%	<20%	85-115%	75-125%	NA	0.01 mg/L
Dissolved organic carbon	<20%	<20%	80-120%	75-125%	NA	0.5 mg/L

*Surrogate recoveries are compound-specific.

† Based on the analysis of #2 Diesel (CAS#: 68476-34-6).

‡ Based on the analysis of gasoline (CAS#: 86290-81-5).

LCS: Lab Control Sample.

The MQOs for the parameters to be measured in the field are shown in Table 7.

Table 7. Measurement quality objectives for Hydrolab calibration checks.
Values indicate the difference, shown as absolute or percentage values, between measured and calibrated values.

Parameter	Units	Accept	Qualify	Reject
pH	std. units	≤ 0.2	> 0.2 and ≤ 0.8	> 0.8
Conductivity*	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

*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%.

6.2.1.1 Precision

Precision is a measure of variability between results of replicate measurements that is due to random error. Laboratory and field duplicate precision for the water chemistry is detailed in Table 6.

For the interlab study, there are two main measures of precision that will be calculated: the repeatability standard deviation and the reproducibility standard deviation (ASTM, 2019).

The repeatability standard deviation, s_r is calculated using the following equation:

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

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

The precision statistics are then compared with critical values of the between-lab consistency to evaluate the performance of the method. The critical values depend on the number of labs participating.

6.2.1.2 Bias

Bias is the difference between the population mean and the true value. Bias is usually addressed by calibrating field and lab instruments, and by analyzing lab control samples, matrix spikes, and/or standard reference materials. The necessary targets for the water chemistry samples are listed in Table 6. An important part of the existing SGC method that addresses bias during analysis of some heavier hydrocarbons is detailed below:

"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 utilize standards which have undergone the cleanup technique to calibrate the GC." (pg. 24; Ecology, 1997)

6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance. It is commonly described as a detection limit. The reporting limits for the water chemistry analysis are listed in Table 6.

Note that the reporting limit or practical limit of quantitation listed in Table 6 for DRO (0.15 mg/L) is lower than that referenced in the TCP guidance (0.5 mg/L).

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

For comparability, the following SOPs and standards will be used:

- Standard Operating Procedure EAP052, Version 1.2: Standard Operating Procedure for Manual Well-Depth and Depth-to-Water Measurements (Marti, 2016a)
- Standard Operating Procedure EAP078, Version 2.1: Standard Operating Procedure for Purging and Sampling Monitoring Wells plus Guidance on Collecting Samples for Volatiles and other Organic Compounds (Marti, 2016b)
- ASTM E691-19: Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method (ASTM, 2019)

6.2.2.2 Representativeness

The previous work by Hobbs et al. (2020) has established that the target study site has groundwater impacted by DRO. Furthermore, the DRO contains a large proportion of polar compounds or metabolites, making it representative of weathered DRO where SGC would be used.

6.2.2.3 Completeness

The project will be considered complete if 95% of the samples are successfully collected and analytical results of those samples meet the project MQOs.

6.3 Acceptance criteria for quality of existing data

All existing data for the study site and groundwater impacted by DRO met the MQOs for the previous study (Hobbs et al., 2020).

6.4 Model quality objectives

Not Applicable

7.0 Study Design

7.1 Study boundaries

We will use the same sample location as the previous study, where DRO in groundwater has already been characterized.

7.2 Field data collection

7.2.1 Sampling locations and frequency

The same field site used to provide contaminated groundwater for the previous study (Hobbs et al., 2020) will be used in this study. All sites used in the previous study are active TCP cleanup sites and the locations remained blind so as not to disrupt the current site cleanups. One sampling event will be necessary to collect sufficient groundwater for the study.

7.2.2 Field parameters and laboratory analytes to be measured

See Tables 6 and 7.

7.3 Modeling and analysis design

Not Applicable

7.4 Assumptions underlying design

The assumptions underlying the project are (1) the study site continues to have weathered DRO contaminated groundwater at the time of sampling, and (2) the project can engage a sufficient number of accredited regional laboratories. Possible challenges associated with these assumptions are discussed in the next section.

7.5 Possible challenges and contingencies

7.5.1 Logistical problems

Previous samples from the on-site monitoring well have shown DRO concentrations in groundwater that vary seasonally. The timeline of this project should enable us to repeat field sampling events if needed to capture sufficient DRO.

7.5.2 Practical constraints

We are relying on the participation of regional accredited laboratories to provide feedback on their use of the NWTPH-Dx method. The strength of an improved method and SGC step will rely on lab participation. It is unknown how receptive labs will be to assist Ecology on this project. Furthermore, when MEL produces a revised SOP or methods document for the SGC, it is unknown whether labs will be willing to follow it. Because we are not under any schedule limitations for this project, we expect to be able to work with the contract labs on any possible methodological issues.

7.5.3 Schedule limitations

There should be no schedule limitations for this project. Sampling of the groundwater will require one field sampling event and the dates are flexible.

The bulk groundwater sample will be stored at the Environmental Assessment Program's Operations Center for subsampling and distribution to participating laboratories. Sample holding times for the subsamples will begin when the subsamples are taken from the large volume bulk groundwater collection.

8.0 Field Procedures

8.1 Invasive species evaluation

Not Applicable

8.2 Measurement and sampling procedures

Static water levels will be measured in the monitoring well upon arriving at the site. Water levels will also be measured during the purging process to ensure that the well is not being over pumped. For optimal sampling, the drawdown should not exceed 0.3 ft. Measurements will be collected according to SOP EAP052 (Marti 2016a).

The monitoring well will be purged and sampled using industry standard low-flow sampling techniques. The well will be purged at a rate of less than 0.5 L/minute using dedicated tubing. The well will be purged through a continuous flow cell until field parameters stabilize (pH, temperature, specific conductance, dissolved oxygen, and oxidation reduction potential) as specified in SOP EAP078 (Marti 2016b).

Screening samples will be collected from the monitoring wells directly from the pump discharge line after they are fully purged. Samples will be stored on ice and transported to the lab within analytical holding times.

Following collection of the screening samples, about 150 L of groundwater will be collected into 45 gallon HDPE drum, with a Teflon liner. This water will be stored in the chain-of-custody cold room at the Environmental Assessment Program (EAP) Operations Center for subsampling throughout the project.

During the *Interlaboratory Study* portion of the project, subsamples of the groundwater with be taken for analysis of DRO. Water will be mixed with a solvent-cleaned stainless steel paddle and sampled using a decontaminated stainless steel jug. Samples will then be preserved and immediately shipped to MEL or a contract lab. The two week analytical hold time for preserved DRO samples will begin at the time of subsampling.

8.3 Containers, preservation methods, holding times

Table 8 lists the parameters of interest for this study. Filtered samples will be field-filtered using a clean standard or high capacity in-line 0.45-micron membrane filter. Samples are listed in the order of sample collection.

8.4 Equipment decontamination

The E-tape probe will be washed in a laboratory grade detergent and water, followed by a clean water rinse, then a deionized water rinse. Any pumps placed in a well will be washed in a laboratory-grade detergent, followed by a tap water rinse and a deionized water rinse. Pump tubing will be dedicated to each well and not reused. Stainless steel equipment used to mix and subsample the collection of groundwater from the holding drum will be washed in a laboratory-grade detergent, followed by a tap water rinse, a deionized water rinse and wrapped in aluminum foil prior to use.

Table 8. Sample containers, preservation, and holding times.

Parameter	Matrix	Container	Preservative	Holding Time
NWTPH-Dx & EPH	water	1 L amber glass bottle	1:1 HCl, cool to ≤6°C	14 days
NWTPH-Gx w/ BTEX & VPH	water	(3) 40 mL vials w/septum	1:1 HCl, cool to ≤6°C	14 days
PAHs	water	1 L amber glass bottle	cool to ≤6°C	7 days
Nitrate-nitrite and ammonia	water	125 mL HDPE	1:1 H_2SO_4, cool to ≤6°C	28 days
Major anions	water	500 mL HDPE bottle	cool to ≤6 °C	28 days
Major cations	water	500 mL HDPE bottle; field filtered	1:1 HNO_3, cool to ≤6°C	6 months
Hardness	water	125 mL HDPE	1:1 H_2SO_4, cool to ≤6°C	6 months
Dissolved organic carbon	water	125 mL HDPE	1:1 HCl, cool to ≤6°C	28 days

BTEX = Benzene-Toluene-Ethylbenzene-Xylenes

8.5 Sample ID

MEL will create sample IDs for the contract lab samples.

8.6 Chain of custody

The bulk collection of DRO contaminated groundwater used in the study will be stored at 4°C in the locked chain-of-custody room in EAP's Operations Center. Subsamples will be taken immediately prior to shipping to the MEL or the contract labs for submission. Sample chain-of-custody and submission will be overseen by Ecology with the contract lab.

8.7 Field log requirements

Field notes taken in the field for the groundwater sampling will follow SOP EAP078 (Marti 2016b).

8.8 Other activities

The bulk collection of groundwater will be stored in a Teflon-lined 45 gallon drum for the duration of the project. Periodic subsampling of the water will require homogenization of the bulk collection using a stainless steel paddle. A stainless steel beaker will then be used to subsample and transfer the groundwater to the pre-acidified sample jar.

9.0 Laboratory Procedures

9.1 Lab procedures table

The laboratory methods for water chemistry are described in Table 9.

Table 9. Laboratory measurement methods.

Analyte	Sample matrix	Number of samples	Expected range of results	Reporting limit	Sample prep method	Analytical (instrumental) method
NWTPH-Dx	water	135	500–10,000 µg/L	500 µg/L	SW3535 and SGC or EPA 3510	NWTPH-Dx
NWTPH-Gx	water	2	250–10,000 µg/L	250 µg/L	SW5030B	NWTPH-Gx
BTEX‡	water	2	1–1000 µg/L	1.0–2.0 µg/L	SW5030B	SW8021B
Polynuclear aromatic hydrocarbons‡	water	2	0.5–500 µg/L	0.05 µg/L	SW3510C	SW8270E w/SIM
Volatile petroleum hydrocarbons	water	2	50–500 µg/L	50 µg/L	SW5030B	WDOE-VPH
Extractable petroleum hydrocarbons	water	2	40–5000 µg/L	40 µg/L	SW3510C	WDOE-EPH
Hardness	water	2	0.3–200 mg/L	0.3 mg/L	NA	SM2340B
Major cations‡	water	2	0.025–500 mg/L	0.025-0.25 mg/L	EPA 200.7	EPA 200.7
Major anions‡	water	2	0.1–500 mg/L	0.1–0.3 mg/L	NA	EPA 300.0
Nitrate-nitrite	water	2	0.01–100 mg/L	0.01 mg/L	NA	SM4500-NO3I
Ammonia	water	2	0.01–2.0 mg/L	0.01 mg/L	NA	SM4500 NH3H
Dissolved organic carbon	water	2	0.5–5 mg/L	0.5 mg/L	NA	SM5310B

‡reporting limits are compound-specific (see Table 6).

9.2 Sample preparation method(s)

Laboratory preparation methods for the water chemistry are listed in Table 9.

9.3 Special method requirements

One of the goals of this study is to evaluate the cleanup methods used during the NWTPH-Dx method for groundwater.

9.4 Laboratories accredited for methods

There are about 25 labs in Washington, Oregon, and Idaho that are accredited for the NWTPH-Dx method in non-potable waters (e.g. groundwater). These labs will be contacted for this study. All other parameters will be analyzed at Manchester Environmental Laboratory (MEL).

Table 10: List of regional laboratories accredited for the NWTPH-Dx method.

State	City	Laboratory Name
WA	Kirkland	Accu Laboratory, LLC
WA	Everett	ALS Environmental - Everett
WA	Kelso	ALS Environmental - Kelso
WA	Kirkland	AmTest Laboratories
WA	Tukwila	Analytical Resources, Inc.
ID	Moscow	Anatek Labs, Inc. - Moscow
WA	Spokane	Anatek Labs, Inc. - Spokane
OR	Tigard	Apex Laboratories, LLC
WA	Vancouver	BSK Associates - Vancouver
WA	Tumwater	Dragon Analytical Laboratory, Inc.
WA	Burlington	Edge Analytical, Inc.
WA	Olympia	ESN Northwest, Inc.
WA	Renton	ESN Northwest, Inc. - Renton
WA	Ferndale	Exact Scientific Services, Inc.
WA	Seattle	Fremont Analytical, Inc.
WA	Seattle	Friedman & Bruya, Inc.
WA	Seattle	King County Environmental Laboratory
WA	Olympia	Libby Environmental, Inc.
WA	Redmond	OnSite Environmental, Inc.
OR	Clackamas	Specialty Analytical
WA	Tacoma	Spectra Laboratories, LLC
WA	Tacoma	Tacoma Environmental Services Laboratory
WA	Tacoma	TestAmerica Seattle-Tacoma
WA	Spokane Valley	TestAmerica Spokane
WA	Tacoma	Water Management Laboratories, Inc.
WA	Port Orchard	Manchester Environmental Lab

10.0 Quality Control Procedures

Communication among the project manager, contract lab, and MEL during the initial stages of the project will ensure the water chemistry results are meeting the project quality control measures.

10.1 Table of field and laboratory quality control

Table 11. Quality control samples, types, and frequency.

Parameter	Field	Laboratory			
	Replicates	Blank spikes	Method blanks	Analytical duplicates	Matrix spikes
NWTPH, VPH/EPH	10% of total samples	2/batch	1/batch	2/batch	NA
BTEX and PAHs	10% of total samples	2/batch	1/batch	1/batch	1/batch
Anions, cations, nutrients and hardness	10% of total samples	1/batch	1/batch	1/batch	1/batch (10% per batch for hardness)

10.2 Corrective action processes

A number of DQOs are built into the initial stages of this project. Continued evaluation and communication among project personnel will ensure that corrective actions (e.g. re-analysis of samples) are taken, if necessary. A laboratory contingency of 20% is built into the project budget to accommodate corrective actions.

11.0 Data Management Procedures

11.1 Data recording and reporting requirements

Field notes during groundwater sampling will be used to document adherence to the sampling SOP EAP078 (Marti 2016b). Lab bench sheets and results from the revision of the NWTPH-Dx method by MEL will be incorporated into the draft SOP or method addendum for review by the participating contract labs.

11.2 Laboratory data package requirements

The water chemistry lab data package will be generated by MEL and the contract lab data packages will be reviewed by MEL. Project data packages will include: a narrative discussing any problems encountered in the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. Quality control results will be evaluated by MEL (discussed below in *Section 13.0 Data Verification*).

The following data qualifiers will be used:

- "J" – The analyte was positively identified. The associated numerical result is an estimate.
- "UJ" – The analyte was not detected at or above the estimated reporting limit.
- "U" – The analyte was not detected above the reporting limit.
- "NJ" – The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.

The qualifiers will be used in accordance with the method reporting limits such that:

- For non-detect values, the estimated detection limit (EDL) is recorded in the "Result Reported Value" column, and a "UJ" is recorded in the "Result Data Qualifier" column.
- Detected values that are below the quantitation limits are reported and qualified as estimates ("J").

11.3 Electronic transfer requirements

All water chemistry lab data will be accessed and downloaded from MEL's Laboratory Information Management System (LIMS) into Excel spreadsheets. MEL will provide an electronic data deliverable (EDD).

11.4 EIM/STORET data upload procedures

The data generated during this project will not be entered into EIM.

11.5 Model information management

Not Applicable.

12.0 Audits and Reports

12.1 Field, laboratory, and other audits

There is no defined audit for the field work in this project.

Ecology's Environmental Laboratory Accreditation Program evaluates a lab's quality system, staff, facilities and equipment, test methods, records, and reports. It also establishes that the lab is capable of providing accurate, defensible data. All assessments are available from Ecology upon request, including MEL's internal performance and audits.

12.2 Responsible personnel

No audits will be conducted during this project.

12.3 Frequency and distribution of reports

At the end of the project, one final report will summarize the results for Ecology's TCP Policy and Technical Support Unit. The report will be accessible on Ecology's *Reports and Publications* webpage.

12.4 Responsibility for reports

The final report will be co-authored by William Hobbs and Joan Protasio.

13.0 Data Verification

13.1 Field data verification, requirements, and responsibilities

Field data will be verified at the time of collection by assistant field staff. As per Marti 2016b all field parameters must meet QC thresholds for stabilization before sampling can occur.

13.2 Laboratory data verification

MEL's QA Coordinator, Christina Frans, will oversee the review and verification of all contract lab data packages, including data flags and qualifiers and chromatography. An EPA Level 2B validation will be requested. All data generated by the contract lab must be included in the final data package. A detailed scope of work for the contract labs will be written by the project manager and MEL's QA Coordinator.

13.3 Validation requirements, if necessary

Not applicable.

13.4 Model quality assessment

Not applicable.

14.0 Data Quality (Usability) Assessment

14.1 Process for determining project objectives were met

The project manager and MEL will determine if the water chemistry data are useable by assessing whether the data have met the MQOs outlined in Table 8. Based on this assessment, the data will either be accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

The objectives of the project will be met following the successful evaluation of the interlaboratory study (as per section *6.2 Measurement quality objectives*) and positive feedback from participating regional accredited labs.

14.2 Treatment of non-detects

There is no specific approach necessary for the treatment of non-detects. The labs will report whether the analyte was not detected at or above the method detection limit or reporting limit, whichever is lower. It is not anticipated that non-detects will be an issue for the parameters being measured.

14.3 Data analysis and presentation methods

The statistical evaluations that will be used in the study have been discussed earlier in section *6.2 Measurement quality objectives*; these follow the ASTM standard E691-19 (ASTM, 2019).

14.4 Sampling design evaluation

The sampling design of the study will be evaluated during the interlaboratory portion of the work based on the adherence to the ASTM standard and the reproducibility of the revised method for the SGC steps in the NWTPH-Dx method.

14.5 Documentation of assessment

Data usability will be described in the *Quality Control* section of the *Results* section in the final report.

15.0 References

ASTM, 2019. Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method. Designation E691-19. West Conshohocken, PA: American Society for Testing and Materials International. Retrieved 1/21/21 from www.astm.org

Ecology, 1997. Analytical Methods for Petroleum Hydrocarbons. Washington State Department of Ecology, Olympia. Publication 97-602. https://apps.ecology.wa.gov/publications/documents/97602.pdf

Ecology. 2016. Guidance for Remediation of Petroleum Contaminated Sites. Publication 10-09-57. Washington State Department of Ecology, Olympia. https://apps.ecology.wa.gov/publications/documents/1009057.pdf

Gough, M., and S. Rowland. 1990. Characterization of unresolved complex mixtures of hydrocarbons in petroleum. Nature 344: 648–650.

Hobbs W.O., C.V. Eickhoff, and K. Lee. 2020. Environmental Effects-Based Concentrations for Weathered Diesel-Range Organics: Toxicity in Marine Water and Freshwater. Publication 20-03-008. Washington State Department of Ecology, Olympia. https://apps.ecology.wa.gov/publications/SummaryPages/2003008.html

Lang, D.A., T.P. Bastow, B.G.K. van Aarssen, B. Warton, G.B. Davis, and C.D. Johnston. 2009. Polar compounds from the dissolution of weathered diesel. Ground Water Monitoring & Remediation 29: 85–93.

Marti, P. 2016a. Standard Operating Procedure EAP052, Version 1.2: Standard Operating Procedure for Manual Well-Depth and Depth-to-Water Measurements. Publication 18-03-215. Washington State Department of Ecology, Olympia. https://apps.ecology.wa.gov/publications/SummaryPages/1803215.html.

Marti, P. 2016b. Standard Operating Procedure EAP078, Version 2.1: Standard Operating Procedure for Purging and Sampling Monitoring Wells plus Guidance on Collecting Samples for Volatiles and other Organic Compounds. Washington State Department of Ecology, Olympia.

Mohler, R. E., Ahn, S., O’Reilly, K., Zemo, D. A., Devine, C. E., Magaw, R., & Sihota, N. (2020). Towards comprehensive analysis of oxygen containing organic compounds in groundwater at a crude oil spill site using GC× GC-TOFMS and Orbitrap ESI-MS. Chemosphere, 244, 125504.

O'Reilly, K.T., R.E. Mohler, D.A. Zemo, S. Ahn, A.K. Tiwari, R.I. Magaw, C. Espino Devine, and K.A. Synowiec. 2015. Identification of ester metabolites from petroleum hydrocarbon biodegradation in groundwater using GCxGC TOFMS. Environmental Toxicology and Chemistry 34:1959–1961.

O'Reilly, K. T., Mohler, R. E., Zemo, D. A., Ahn, S., Magaw, R. I., & Espino Devine, C. 2019. Oxygen-Containing Compounds Identified in Groundwater from Fuel Release Sites Using GCxGC-TOF-MS. Groundwater Monitoring & Remediation, 39(4), 32-40.

U.S. Environmental Protection Agency (USEPA), 1996. SW-846 Test Method 3630C: Silica Gel Cleanup. https://www.epa.gov/hw-sw846/sw-846-test-method-3630c-silica-gel-cleanup

Zemo, D. A., Synowiec, K. A., Magaw, R. I., & Mohler, R. E., 2013. Comparison of shake and column silica gel cleanup methods for groundwater extracts to be analyzed for TPHd/DRO. Groundwater Monitoring & Remediation, 33: 108-112.

16.0 Appendices

Appendix A. Lab Survey for Accredited Labs

Washington State Department of Ecology - NWTPH-Dx Method Survey

1. Ecology is working towards providing updated guidance to the NWTPH-Dx method for the use of silica gel cleanup [3]. Do you have any recommendations on what Ecology should change about the method? Of particular interest is the analysis of groundwater samples – are there recommendations specific to this matrix?

2. Please share your current SOP for the silica gel cleanup of NWTPH-Dx samples, including whether sulfuric acid cleanup is routinely used (EPA3630 or NWTPH-Dx).

3. Please share your current SOP(s) for the NWTPH-Dx method to include extraction, cleanup, and analysis. If you are not comfortable sharing your internal or modified NWTPH-Dx method, please fill in the following information:

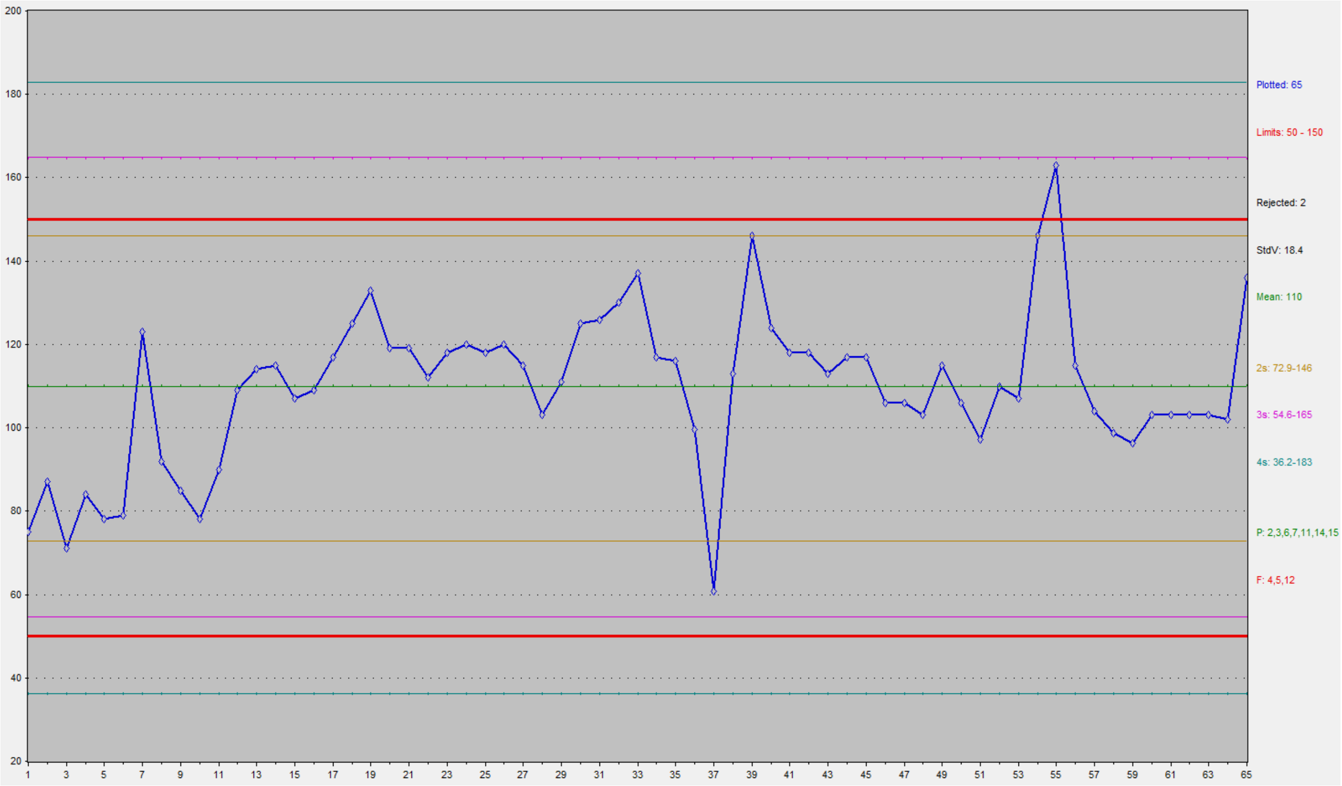
NWTPH-Dx Summary	**Details (*Examples – delete when filling out*)**
Analytical instrument	Agilent 7820 GC with FID
Extraction method solid	Sonication, SW3550C
Extraction method water	Separatory Funnel, SW3510C
Extraction solvent	Methylene Chloride
Cleanup	NWTPH-Dx with free flowing silica gel; sometimes with H_2SO_4
Surrogate standard	Pentacosane
Spiking compound	#2 Diesel Oil
NWTPH-Dx quantification ranges	How do you determine the appropriate integration ranges for reporting diesel and motor oil (e.g. by selecting retention time ranges)?

4. What are your current reporting limits for the NWTPH-Dx method in soil and water? Do you report MDLs and if so what are your current MDLs for soil and water?

5. Please provide a statistical summary of surrogate recoveries for the last 20 sample runs for soil and water. Below is an example graph with numerical statistical summary in the right margin (*delete the example when filling out this form*).

---

[3] Ecology (1997). Analytical Methods for Petroleum Hydrocarbons. Publication No. ECY 97-602, June 1997.



6. Would you be interested in reviewing and providing feedback on any updated guidance that Ecology drafts?

7. Ecology would like to complete a small interlaboratory comparison for the revised guidance on the NWTPH-Dx method with silica gel cleanup. Only labs that are accredited by Ecology for the method will be participating. Labs will be compensated for analysis costs. Would you be interested in participating?

Appendix B. Glossaries, Acronyms, and Abbreviations

Glossary of General Terms

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.

Practical Quantitation Limit (PQL): The lowest concentration that can be reliably measured within specified limits of precision, accuracy, representativeness, completeness, and comparability during routine laboratory operating conditions, using department approved methods (WAC 173-204-200(35)).

Reverse surrogate: a QC measure where a polar compound is injected into the extract to evaluate the effectiveness of the silica gel removal. Zemo et al. (2013) used capric acid.

Silica column: a glass column packed with silica gel; Zemo et al. (2013) used 10g of silica gel.

Silica gel free flowing or shaker method: following NWTPH-Dx method, is adding the silica gel (0.4g) to a centrifuge tube containing the DCM extract.

Sulfuric acid (H_2SO_4) cleanup: the initial step in the NWTPH-Dx method, adding 1ml of concentrated H_2SO_4 to 10ml of sample extract.

Surrogate spike: a QC measure where a non-polar compound is injected into the extract and recovery is measured following SGC.

Acronyms and Abbreviations

DQO	Data quality objective
DRO	Diesel range organics
EAP	Environmental Assessment Program
Ecology	Washington State Department of Ecology
e.g.	For example
et al.	And others
GRO	Gasoline range organics
i.e.	In other words
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
NWTPH-Dx	(see Glossary above)
NWTPH-Gx	(see Glossary above)
PQL	(see Glossary above)
QA	Quality assurance
QC	Quality control
RPD	Relative percent difference
SGC	Silica gel cleanup
SOP	Standard operating procedures
SRM	Standard reference materials
TCP	Toxics Cleanup Program
TPH	Total petroleum hydrocarbon
WAC	Washington Administrative Code
WDOE	Washington State Department of Ecology

Units of Measurement

mg/L	milligrams per liter (parts per million)
µg/L	micrograms per liter (parts per billion)

Quality Assurance Glossary

Accreditation: A certification process for laboratories, designed to evaluate and document a lab's ability to perform analytical methods and produce acceptable data. For Ecology, it is "Formal recognition by (Ecology)…that an environmental laboratory is capable of producing accurate analytical data." [WAC 173-50-040] (Kammin, 2010)

Accuracy: The degree to which a measured value agrees with the true value of the measured property. USEPA recommends that this term not be used, and that the terms *precision* and *bias* be used to convey the information associated with the term *accuracy* (USGS, 1998).

Analyte: An element, ion, compound, or chemical moiety (pH, alkalinity) which is to be determined. The definition can be expanded to include organisms, e.g., fecal coliform, Klebsiella (Kammin, 2010).

Bias: The difference between the sample mean and the true value. Bias usually describes a systematic difference reproducible over time and is characteristic of both the measurement system and the analyte(s) being measured. Bias is a commonly used data quality indicator (DQI) (Kammin, 2010; Ecology, 2004).

Blank: A synthetic sample, free of the analyte(s) of interest. For example, in water analysis, pure water is used for the blank. In chemical analysis, a blank is used to estimate the analytical response to all factors other than the analyte in the sample. In general, blanks are used to assess possible contamination or inadvertent introduction of analyte during various stages of the sampling and analytical process (USGS, 1998).

Calibration: The process of establishing the relationship between the response of a measurement system and the concentration of the parameter being measured (Ecology, 2004).

Check standard: A substance or reference material obtained from a source independent from the source of the calibration standard; used to assess bias for an analytical method. This is an obsolete term, and its use is highly discouraged. See Calibration Verification Standards, Lab Control Samples (LCS), Certified Reference Materials (CRM), and/or spiked blanks. These are all check standards but should be referred to by their actual designator, e.g., CRM, LCS (Kammin, 2010; Ecology, 2004).

Comparability: The degree to which different methods, data sets and/or decisions agree or can be represented as similar; a data quality indicator (USEPA, 1997).

Completeness: The amount of valid data obtained from a project compared to the planned amount. Usually expressed as a percentage. A data quality indicator (USEPA, 1997).

Continuing Calibration Verification Standard (CCV): A quality control (QC) sample analyzed with samples to check for acceptable bias in the measurement system. The CCV is usually a midpoint calibration standard that is re-run at an established frequency during the course of an analytical run (Kammin, 2010).

Control chart: A graphical representation of quality control results demonstrating the performance of an aspect of a measurement system (Kammin, 2010; Ecology 2004).

Control limits: Statistical warning and action limits calculated based on control charts. Warning limits are generally set at +/- 2 standard deviations from the mean, action limits at +/- 3 standard deviations from the mean (Kammin, 2010).

Data integrity: A qualitative DQI that evaluates the extent to which a data set contains data that is misrepresented, falsified, or deliberately misleading (Kammin, 2010).

Data quality indicators (DQI): Commonly used measures of acceptability for environmental data. The principal DQIs are precision, bias, representativeness, comparability, completeness, sensitivity, and integrity (USEPA, 2006).

Data quality objectives (DQO): Qualitative and quantitative statements derived from systematic planning processes that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions (USEPA, 2006).

Data set: A grouping of samples organized by date, time, analyte, etc. (Kammin, 2010).

Data validation: An analyte-specific and sample-specific process that extends the evaluation of data beyond data verification to determine the usability of a specific data set. It involves a detailed examination of the data package, using both professional judgment and objective criteria, to determine whether the MQOs for precision, bias, and sensitivity have been met. It may also include an assessment of completeness, representativeness, comparability, and integrity, as these criteria relate to the usability of the data set. Ecology considers four key criteria to determine if data validation has actually occurred. These are:

- Use of raw or instrument data for evaluation.
- Use of third-party assessors.
- Data set is complex.
- Use of EPA Functional Guidelines or equivalent for review.

Examples of data types commonly validated would be:

- Gas Chromatography (GC).
- Gas Chromatography-Mass Spectrometry (GC-MS).
- Inductively Coupled Plasma (ICP).

The end result of a formal validation process is a determination of usability that assigns qualifiers to indicate usability status for every measurement result. These qualifiers include:

- No qualifier – data are usable for intended purposes.
- J (or a J variant) – data are estimated, may be usable, may be biased high or low.
- REJ – data are rejected, cannot be used for intended purposes.
  (Kammin, 2010; Ecology, 2004).

Data verification: Examination of a data set for errors or omissions, and assessment of the Data Quality Indicators related to that data set for compliance with acceptance criteria (MQOs). Verification is a detailed quality review of a data set (Ecology, 2004).

Detection limit (limit of detection)**:** The concentration or amount of an analyte which can be determined to a specified level of certainty to be greater than zero (Ecology, 2004).

Duplicate samples: Two samples taken from and representative of the same population, and carried through and steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variability of all method activities including sampling and analysis (USEPA, 1997).

Field blank: A blank used to obtain information on contamination introduced during sample collection, storage, and transport (Ecology, 2004).

Initial Calibration Verification Standard (ICV): A QC sample prepared independently of calibration standards and analyzed along with the samples to check for acceptable bias in the measurement system. The ICV is analyzed prior to the analysis of any samples (Kammin, 2010).

Laboratory Control Sample (LCS): A sample of known composition prepared using contaminant-free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern. It is prepared and analyzed in the same batch of regular samples using the same sample preparation method, reagents, and analytical methods employed for regular samples (USEPA, 1997).

Matrix spike: A QC sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias due to interference or matrix effects (Ecology, 2004).

Measurement Quality Objectives (MQOs)**:** Performance or acceptance criteria for individual data quality indicators, usually including precision, bias, sensitivity, completeness, comparability, and representativeness (USEPA, 2006).

Measurement result: A value obtained by performing the procedure described in a method (Ecology, 2004).

Method: A formalized group of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, data analysis), systematically presented in the order in which they are to be executed (USEPA, 1997).

Method blank: A blank prepared to represent the sample matrix, prepared and analyzed with a batch of samples. A method blank will contain all reagents used in the preparation of a sample, and the same preparation process is used for the method blank and samples (Ecology, 2004; Kammin, 2010).

Method Detection Limit (MDL): This definition for detection was first formally advanced in 40CFR 136, October 26, 1984 edition. MDL is defined there as the minimum concentration of an analyte that, in a given matrix and with a specific method, has a 99% probability of being identified, and reported to be greater than zero (Federal Register, October 26, 1984).

Percent Relative Standard Deviation (%RSD): A statistic used to evaluate precision in environmental analysis. It is determined in the following manner:

$$\mathbf{\%RSD = (100 * s)/x}$$

where s is the sample standard deviation and x is the mean of results from more than two replicate samples (Kammin, 2010).

Parameter: A specified characteristic of a population or sample. Also, an analyte or grouping of analytes. Benzene and nitrate + nitrite are all parameters (Kammin, 2010; Ecology, 2004).

Population: The hypothetical set of all possible observations of the type being investigated (Ecology, 2004).

Precision: The extent of random variability among replicate measurements of the same property; a data quality indicator (USGS, 1998).

Quality assurance (QA): A set of activities designed to establish and document the reliability and usability of measurement data (Kammin, 2010).

Quality Assurance Project Plan (QAPP): A document that describes the objectives of a project, and the processes and activities necessary to develop data that will support those objectives (Kammin, 2010; Ecology, 2004).

Quality control (QC): The routine application of measurement and statistical procedures to assess the accuracy of measurement data (Ecology, 2004).

Relative Percent Difference (RPD): RPD is commonly used to evaluate precision. The following formula is used:

$$[Abs(a-b)/((a + b)/2)] * 100$$

where "Abs()" is absolute value and a and b are results for the two replicate samples. RPD can be used only with 2 values. Percent Relative Standard Deviation is (%RSD) is used if there are results for more than 2 replicate samples (Ecology, 2004).

Replicate samples: Two or more samples taken from the environment at the same time and place, using the same protocols. Replicates are used to estimate the random variability of the material sampled (USGS, 1998).

Representativeness: The degree to which a sample reflects the population from which it is taken; a data quality indicator (USGS, 1998).

Sample (field): A portion of a population (environmental entity) that is measured and assumed to represent the entire population (USGS, 1998).

Sample (statistical): A finite part or subset of a statistical population (USEPA, 1997).

Sensitivity: In general, denotes the rate at which the analytical response (e.g., absorbance, volume, meter reading) varies with the concentration of the parameter being determined. In a specialized sense, it has the same meaning as the detection limit (Ecology, 2004).

Spiked blank: A specified amount of reagent blank fortified with a known mass of the target analyte(s); usually used to assess the recovery efficiency of the method (USEPA, 1997).

Spiked sample: A sample prepared by adding a known mass of target analyte(s) to a specified amount of matrix sample for which an independent estimate of target analyte(s) concentration is available. Spiked samples can be used to determine the effect of the matrix on a method's recovery efficiency (USEPA, 1997).

Split sample: A discrete sample subdivided into portions, usually duplicates (Kammin, 2010).

Standard Operating Procedure (SOP): A document which describes in detail a reproducible and repeatable organized activity (Kammin, 2010).

Surrogate: For environmental chemistry, a surrogate is a substance with properties similar to those of the target analyte(s). Surrogates are unlikely to be native to environmental samples. They are added to environmental samples for quality control purposes, to track extraction efficiency and/or measure analyte recovery. Deuterated organic compounds are examples of surrogates commonly used in organic compound analysis (Kammin, 2010).

Systematic planning: A step-wise process which develops a clear description of the goals and objectives of a project, and produces decisions on the type, quantity, and quality of data that will be needed to meet those goals and objectives. The DQO process is a specialized type of systematic planning (USEPA, 2006).

References for QA Glossary

Ecology, 2004. Guidance for the Preparation of Quality Assurance Project Plans for Environmental Studies. Washington State Department of Ecology, Olympia, WA. https://apps.ecology.wa.gov/publications/SummaryPages/0403030.html.

Kammin, B., 2010. Definition developed or extensively edited by William Kammin, 2010. Washington State Department of Ecology, Olympia, WA.

USEPA, 2006. Guidance on Systematic Planning Using the Data Quality Objectives Process EPA QA/G-4. http://www.epa.gov/quality/qs-docs/g4-final.pdf.

USGS, 1998. Principles and Practices for Quality Assurance and Quality Control. Open-File Report 98-636. U.S. Geological Survey. http://ma.water.usgs.gov/fhwa/products/ofr98-636.pdf.