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Addendum to Quality Assurance Project Plan

Environmental Effects–Based Concentrations for Total Petroleum Hydrocarbons (TPH) in Marine Water and Freshwater

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Addendum to Quality Assurance Project Plan

Environmental Effects-Based Concentrations for Total Petroleum Hydrocarbons (TPH) in Marine Water and Freshwater

April 2019

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Signatures are not available on the Internet version.
EAP: Environmental Assessment Program
MEL: Manchester Environmental Laboratory
TCP: Toxics Cleanup Program
WQP: Water Quality Program

Table of Contents

List of Figures

List of Tables

3.0 Background

3.1 Introduction and problem statement

The Washington State Department of Ecology (Ecology) Toxics Cleanup Program (TCP) is responsible for identifying and remediating sites impacted by hazardous substances. In 2018 TCP commissioned a study that defined environmental effects–based concentrations for aquatic organisms exposed to total petroleum hydrocarbons (referred to as *Northwest TPH* or *NWTPH* after the lab method) (Hobbs et al. 2018). Using the effects-based concentrations, the TCP's Policy and Technical Support Unit then wrote an implementation memorandum, recommending protective values under WAC 173-340-730(3)(b)(ii) (Environmental effects) – Surface Water Cleanup Standards. This memorandum is currently under review.

The previous Ecology study defined clear lethal and sublethal effects concentrations (Table 1). A laboratory-based toxicity test dilution series for NWTPH-Dx (diesel fraction) and NWTPH-Gx (gasoline fraction) was used to determine the no observed effect concentration (NOEC) and lowest observed effect concentration (LOEC) for two marine and two freshwater organisms. Certified reference standards for diesel fuel and gasoline were used to create the dilution series in the lab. This allowed Ecology to create precise dilution series concentrations and eliminate other contaminants that would be present in field collections of contaminated waters. Hobbs et al. (2018) recommended a companion field study to establish effects-based concentrations using contaminated groundwater and weathered diesel-range organics (DRO) as defined by NWTPH-Dx.

The goal of this follow-up study is to establish effects-based concentrations (NOEC and LOEC) for aquatic organisms in freshwater and marine waters on weathered DRO. Weathered DRO will be collected in contaminated groundwater. Based on the findings from the previous study, the contaminated groundwater should have concentrations of NWTPH-Gx <1000 µg/L. The study design for toxicity testing and observed effects–based concentrations will follow the original Quality Assurance Project Plan (QAPP) (Hobbs 2017). This QAPP addendum details the recovery and screening of the contaminated groundwater for use in the toxicity tests. Only those sections that differ from the original QAPP are included in the addendum.

Table 1. Toxicity point estimates and effects concentrations for unweathered NWTPH in marine water and freshwater (Hobbs et al. 2018).

		Point Estimates (mg/L)		LOEC (mg/L)	NOEC (mg/L)
		LC50	IC25		
NWTPH-Gx	Marine water	1.7	1.7	>1.7	1.7
	Freshwater	2.5	1.5	2.1	1.0
NWTPH-Dx	Marine water	0.68	0.19	0.05	<0.05
	Freshwater	0.23	0.17	0.22	0.15

LC = Lethal Concentration; IC = Inhibition Concentration; NOEC = No Observed Effect Concentration; LOEC = Lowest Observed Effect Concentration.

3.2 Study area and surroundings

Ecology will identify two sites undergoing Model Toxics Control Act (MTCA) cleanup that have groundwater contaminated by DRO. Based on previous investigations by TCP and landowners in Washington State, there are a number of candidate sites (San Juan 2014, 2015). In addition, Ecology will collaborate with toxicologists at Chevron Corporation to assist in identifying possible sites with contaminated groundwater. Potential sites will be screened for a range of contaminants to assess whether DRO (as defined by the NWTPH-Dx lab method) is the predominant contaminant for toxicity testing.

3.2.1 History of study area

One potential site has been identified in Everett. The site of a former bulk fuel terminal, currently owned by ExxonMobil–American Distributing Company, has had a history of fuel releases into surrounding soils and groundwater. Site operations began in 1927 and continued until 1990. Site investigations and cleanup have been underway at the site since 1996. Ecology's TCP oversees the MTCA cleanup activities at this site (Cleanup Site ID# 5182). The current remedial approach is groundwater-monitored natural attenuation.

A second potential site is a former petroleum service station located in Seattle (Cleanup Site ID# 6439). This site is currently leased as a tow yard facility. In 2013, TCP conducted a Site Hazard Assessment and concluded there was a low relative risk from hydrocarbon contamination at the site (Musa, 2013). There is contamination of the soils and groundwater by diesel and gasoline fuels.

3.2.2 Summary of previous studies and existing data

In 2015, San Juan (2015) completed a detailed analysis of the site groundwater and soil petroleum footprint on the ExxonMobil site. There is an extensive plume of diesel-contaminated groundwater. Monitoring wells within this plume have shown a decrease in concentrations over time (Figure 1). The previous data from the monitoring wells also describes how NWTPH-Dx is much more predominant compared to the gasoline fraction (NWTPH-Gx), the latter being less than the analytical reporting limits in some cases. This potential study site also has a groundwater well where concentrations of NWTPH are routinely below the analytical reporting limits. This well could act as a proximal (on-site) control well (MWA7 shown in Figure 1). Data from this site was accessed through Ecology's Environmental Information Management (EIM) system.

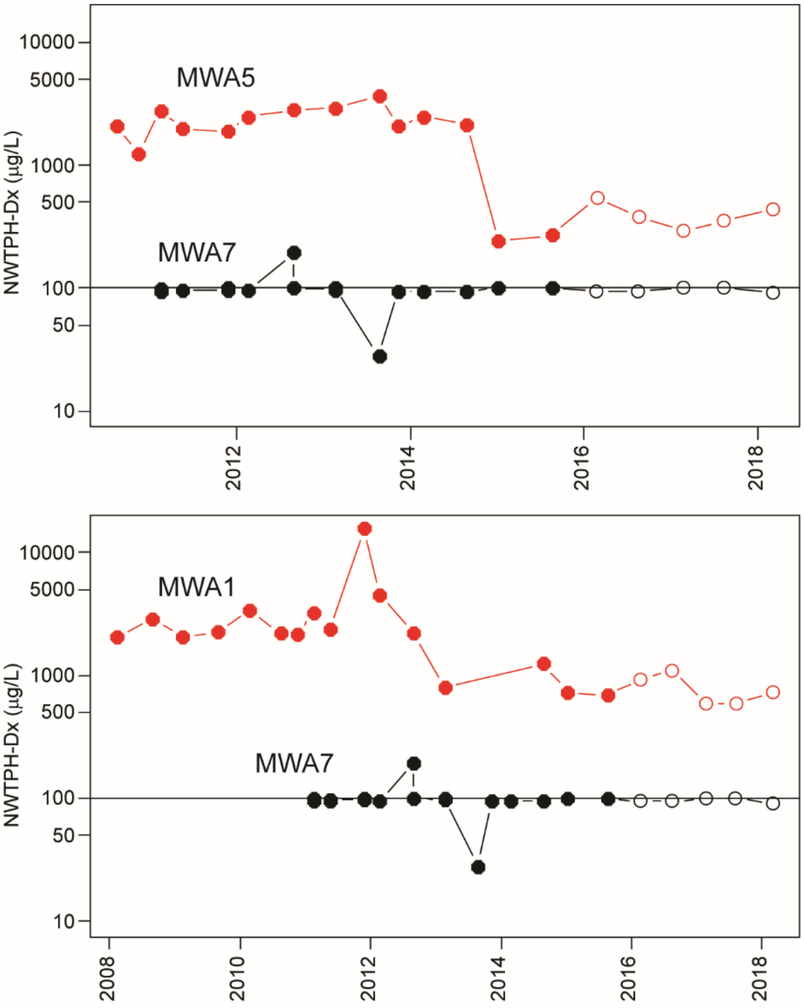

Figure 1. Trends of NWTPH-Dx in groundwater at the ExxonMobil site.
—*Above*, concentrations of NWTPH-Dx sampled in MWA5 relative to the proposed on-site control well MWA7. —*Below*, concentrations in MWA1. Closed circles are samples analyzed by method NWTPH-Dx and open circles are samples analyzed using SW8015-M. Y-axis is a logarithmic scale. The solid horizontal line is the method detection limit for NWTPH-Dx (100 µg/L). Silica gel cleanup of the samples was not conducted.

The second candidate site has also had a history of measured NWTPH-Dx concentrations in groundwater that are above 1000 µg/L, with NWTPH-Gx concentrations that are less than 1000 µg/L (Figure 2). It is currently unknown whether a suitable on-site control well exists at or near this site.

Figure 2. Trend over time for NWTPH-Dx in groundwater at a former Seattle service station.
Y-axis is a logarithmic scale.

3.2.3 Parameters of interest and potential sources

This study is focused on weathered DRO, which includes weathered diesel fuel- and 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. Aged diesel fuels in the groundwater will contain concentrations of dissolved petroleum-derived chemicals. These degradation products are 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, but many of the compounds are still referred to as an “unresolved complex mixture” (Gough and Rowland 1990). Generally, as the products oxidize and carbon chains are broken and transformed there is a shift towards heavier compounds and longer elution times during analysis (Figure 3). Guidance by 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 NWTPH.

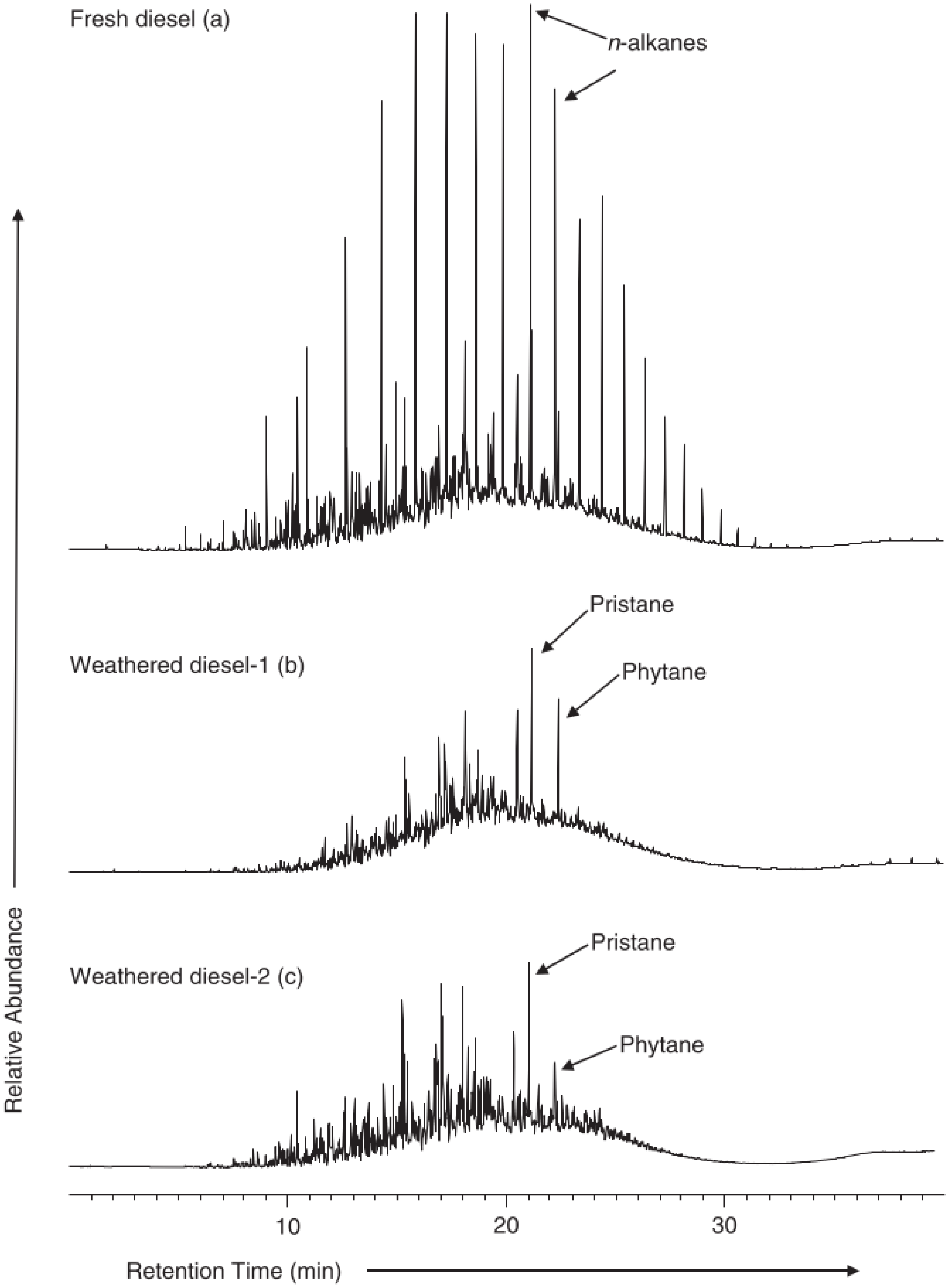

Figure 3. Gas chromatograph of fresh (a) and weathered (b and c) diesel fuel (Lang et al. 2009). The highlighted compound peaks on the chromatograms describe the degradation of n-alkanes to resistant compounds of pristane and phytane.

The ecological toxicity of petroleum metabolites is not clearly defined. Some research suggests a measurable toxicity of certain petroleum metabolites (Barron et al. 1999; Scarlett et al. 2012; Hellmann-Blumberg et al. 2016), while other researchers have made the case that toxicity is low for most petroleum metabolites (Zemo et al. 2013; O'Reilly et al. 2015). This follow-up project does not explicitly address the presence or potential toxicity of petroleum metabolites.

In order to confirm that NWTPH-Dx is the predominant contaminant present in groundwater, screening samples will be analyzed for a number of additional parameters (Table 2). These parameters will also assist in characterizing the ionic chemistry of the groundwater, to allow for the amendment of the water and testing of both marine and freshwater organisms.

Table 2: Parameters for screening samples.

Organics	Inorganics
NWTPH and benzene, toluene, ethylbenzene, and xylenes (BTEX)	Metals (arsenic, silver, thallium, beryllium, cadmium, chromium, copper, mercury, lead, nickel, selenium, antimony, and zinc)
Volatile and extractable petroleum hydrocarbons	Major ions (sodium, magnesium, potassium, calcium, sulfate, nitrate-nitrite, chloride, fluoride, and bromide) and total dissolved solids
Polynuclear aromatic hydrocarbons	Sulfides and ammonia
Dissolved organic carbon	pH, conductivity, and dissolved oxygen (field)
	Hardness and alkalinity

4.0 Project Description

4.1 Project goal

The project goal is to produce environmental effects–based NOEC and LOEC concentrations of weathered diesel-range hydrocarbons that can be used to propose numerical cleanup levels protective of aquatic life in marine water and freshwater pursuant to WAC 173-340-730(3)(b)(ii).

4.2 Project objectives

The project objectives include:

- Collect and screen contaminated groundwater to confirm that NWTPH-Dx is the predominant contaminant.
- Supervise a laboratory-based series of toxicity tests using weathered diesel to determine the NOEC and LOEC on two freshwater and two marine organisms.
- Enter data into EAP's Comprehensive Environmental Toxicity Information System (CETIS) database. Water chemistry data should also be entered into the EIM database.
- Analyze the toxicity test data to establish a statistically defendable NOEC and LOEC for NWTPH-Dx in marine and freshwater.

4.4 Tasks required

The project tasks include:

- Write addendum to the original QAPP (Hobbs 2017).
- Identify and sample potential groundwater wells contaminated with NWTPH-Dx.
- Screen the chemistry of the potential study sites. Analyses will be conducted by Ecology's Manchester Environmental Laboratory (MEL).
- Identify sampling and control wells. Pump sufficient groundwater to conduct all toxicity testing and ship to Nautilus Environmental.
- Conduct both range-finding and final chronic toxicity tests on freshwater and marine organisms. Confirm the NWTPH-Dx concentration of the bioassay water throughout the tests.
- Receive and analyze the bioassay data in CETIS to establish the NOEC and LOEC concentrations.
- Write the final report.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 3. Organization of project staff and responsibilities.

Staff	Title	Responsibilities
Arthur Buchan TCP Phone: 360-407-7146	EAP Client	Clarifies scope of the project. Provides internal review of the QAPP addendum, approves the budget, and approves the final QAPP addendum.
William Hobbs TSU-SCS-EAP Phone: 360-407-7512	Project Manager	Writes the QAPP addendum and Sole Source Lab Contract. Oversees bioassay design by contract laboratory. Assists with groundwater sampling. Conducts QA review of data, analyzes and interprets data. Writes the draft report and final report.
Chris Dudenhoeffer WQP Phone: 360-407-6445	Project Scientist	Reviews QAPP addendum. Conducts QA review of data, analyzes and interprets data.
Pam Marti GWFF-SCS-EAP Phone: 360-407-6432	Project Scientist	Leads sampling of groundwater wells for screening and retrieval of toxicity test waters.
Charles San Juan TCP Phone: 360-407-7191	Project Scientist	Assists in site selection. Provides internal review of the QAPP addendum and project scope.
John Weakland MEL Phone: 360-871-8820	Project Scientist	Provides internal review of the QAPP addendum and project scope. Oversees sample chemical analysis and interpretation of chromatograms.
Debby Sargeant TSU-SCS-EAP Phone: 360-407-6775	Unit Supervisor for the Project Manager	Provides internal review of the QAPP addendum, approves the budget, and approves the final QAPP addendum.
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 addendum, and approves the final QAPP addendum.
Alan Rue MEL-EAP Phone: 360-871-8801	Director, MEL	Reviews and approves the final QAPP addendum.
Curtis Eickhoff Nautilus Environmental Phone: 604-420-8773	Project Manager	Reviews draft QAPP addendum, coordinates with MEL QA Coordinator, oversees toxicity tests and reporting.
Arati Kaza Phone:360-407-6964	Ecology Quality Assurance Officer	Reviews the draft QAPP addendum and approves the final QAPP addendum.

TCP: Toxics Cleanup Program; TSU: Toxics Studies Unit; SCS: Statewide Coordination Section; GWFF: Groundwater, Forests and Fish Unit; EAP: Environmental Assessment Program; WQP: Water Quality Program; EIM: Environmental Information Management database; QAPP: Quality Assurance Project Plan; MEL: Manchester Environmental Laboratory.

5.4 Proposed project schedule

Table 4. Proposed schedule for completing field and laboratory work, data entry, and reports.

Work category	Work description	Due date	Lead staff / support staff
Field and laboratory work	Field work completed	March 2019	William Hobbs
	Lab analyses completed (MEL)	June 2019	John Weakland
	Lab analyses completed (contract)	June 2019	Curtis Eickhoff
CETIS database (Study ID WHOB009)	CETIS data loaded	September 2019	Chris Dudenhoeffer
Environmental Information System (EIM) database (Study ID WHOB009)	EIM data loaded	August 2019	TBD
	EIM data entry review	September 2019	Siana Wong
	EIM complete	October 2019	TBD
Final report	Draft due to supervisor	September 2019	William Hobbs, John Weakland, and Curtis Eickhoff
	Draft due to client/peer reviewer	October 2019	William Hobbs, John Weakland, and Curtis Eickhoff
	Final (all reviews done) due to publications coordinator	November 2019	William Hobbs, John Weakland, and Curtis Eickhoff
	Final report due on web	December 2019	William Hobbs, John Weakland, and Curtis Eickhoff

5.5 Budget and funding

The detailed laboratory budget for the project is shown in Table 5. The total project budget is $116,979.

Table 5. Project budget and funding.

Project stage	Number of samples	Number of QA samples	Total number of samples	Cost per sample	Lab subtotal
Screening Samples					
NWTPH, metals, PAH, general chemistry	5	2	7	$1,200	$8,400
Toxicity testing					
Mixing	5	1	6	$140	$840
Range-finding	50	5	55	$120	$6,600
Final chronic toxicity tests	100	10	110	$120	$13,200
VPH/EPH	10	2	12	$375	$4500
MEL Subtotal					$33,540
Contract Lab Subtotal					$35,000
Lab Grand Total					$68,540
Budget Items					Estimated Cost
Salary and benefits					$48,439
Contracts (Bioassay contract lab)					$35,000
Laboratory (MEL)					$33,540
Project Total					$116,979

6.0 Quality Objectives

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†	<40	<40	70-130	70-130	50-150	0.15 mg/L
NWTPH-Gx‡	<50	<40	70-130	70-130	70-130	0.07 mg/L
Volatile petroleum hydrocarbons	<30	<30	70-130	70-130	70-130	50 µg/L
Extractable petroleum hydrocarbons	<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
Total dissolved carbon	<30	NA	80-120	NA	NA	0.5 mg/L
Polynuclear aromatic hydrocarbons						
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
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(ghi)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

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
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	<30	<30	85-115	75-125	70-130	0.025 mg/L
Magnesium	<30	<30	85-115	75-125	70-130	0.025 mg/L
Potassium	<30	<30	85-115	75-125	70-130	0.25 mg/L
Calcium	<30	<30	85-115	75-125	70-130	0.025 mg/L
Sulfate	<30	<30	90-110	75-125	70-130	0.30 mg/L
Nitrate-nitrite	<30	<30	80-120	75-125	70-130	0.01 mg/L
Chloride	<30	<30	90-110	75-125	70-130	0.10 mg/L
Bromide	<30	<30	90-110	75-125	70-130	0.025 mg/L
Fluoride	<30	<30	90-110	75-125	70-130	0.10 mg/L
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
Metals						
Arsenic (As)	<30	<30	85-115	75-125	70-130	0.10 µg/L
Silver (Ag)	<30	<30	85-115	75-125	70-130	0.02 µg/L
Antimony (Sb)	<30	<30	85-115	75-125	70-130	0.20 µg/L
Beryllium (Be)	<30	<30	85-115	75-125	70-130	0.10 µg/L
Cadmium (Cd)	<30	<30	85-115	75-125	70-130	0.02 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
Chromium (Cr)	<30	<30	85-115	75-125	70-130	0.10 µg/L
Copper (Cu)	<30	<30	85-115	75-125	70-130	0.10 µg/L
Mercury (Hg)	<30	<30	80-120	75-125	70-130	0.05 µg/L
Lead (Pb)	<30	<30	85-115	75-125	70-130	0.20 µg/L
Nickel (Ni)	<30	<30	85-115	75-125	70-130	0.10 µg/L
Selenium (Se)	<30	<30	85-115	75-125	70-130	0.10 µg/L
Thallium (Tl)	<30	<30	85-115	75-125	70-130	0.10 µg/L
Zinc (Zn)	<30	<30	85-115	75-125	70-130	1.00 µg/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.

Parameter	Units	Accept	Qualify	Reject
pH	std. units	< or = ± 0.2	> ± 0.2 and < or = ± 0.8	> ± 0.8
Conductivity*	µS/cm	< or = ± 5	> ± 5 and < or = ± 15	> ± 15
Temperature	°C	< or = ± 0.2	> ± 0.2 and < or = ± 0.8	> ± 0.8
Dissolved oxygen	mg/L	< or = ± 0.3	> ± 0.3 and < or = ± 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 criteria of less than 5%.

7.0 Study Design

7.2 Field data collection

7.2.1 Sampling location and frequency

The goal of this study is to determine effects-based concentrations of weathered NWTPH-Dx on aquatic organisms. We are using groundwater that is impacted by historical diesel fuel contamination to achieve the study goal. Currently the most promising potential location is an ExxonMobil property that is undergoing a MTCA cleanup (CSID# 2728). On this property there are a few wells located in a plume of Dx-contaminated groundwater (AMEC, 2011). We will screen two of the wells that have concentrations of NWTPH-Dx above 1,000 µg/L and NWTPH-Gx concentrations less than analytical detection limits (250 µg/L).

On this property there is also a suitable control well, where concentrations of NWTPH and other individual hydrocarbon compounds are routinely less than the analytical detection limits. This well will be screened and water used as a control. By using on-site groundwater that lacks detectable NWTPH-Dx as a control in the toxicity testing, we will be incorporating any effect that naturally occurring organics might have on the organisms. Any observable effect is therefore attributable to diesel-range organics or metabolites of diesel-range organics.

Two site visits will be necessary: one to collect the screening samples and one to pump the water for toxicity testing. The approach to sampling the study sites will be the same for all potential sites.

7.5 Possible challenges and contingencies

7.5.1 Logistical problems

The success of this project relies on being able to access a contaminated site and attain a sufficient volume of groundwater contaminated with NWTPH-Dx. To facilitate site access, TCP is working closely with landowners. There are a number of potential sites that could be screened, should the Exxon/Mobil site not be accessible.

Being able to pump and ship the required volume of water for toxicity testing is not viewed as a problem, but it will require advance planning for containers and shipping. Previous studies have successfully shipped 20-L samples to Canadian environmental labs.

7.5.2 Practical constraints

The groundwater used in this study will be sampled at the same time and shipped to the lab in aliquots. The period of time between sampling and use in the toxicity tests will be beyond the analytical holding time for NWTPH-Dx, which is 7 days (unpreserved). This means that the chemistry of our study water will likely change. To constrain this and to ensure that the organisms are being exposed to known concentrations, sufficient samples of the study water will be analyzed before and during the tests. The frequency of analysis will follow the previous study (Hobbs 2018).

There are also possible constraints in using the same freshwater invertebrate as in the previous toxicity tests (see *Section 9.2 Sample Preparation Methods*). Should the approach being used in this study prove to be ineffective, a different freshwater invertebrate will be used: *Daphnia magna*. The replacement *Daphnia* has been shown to be less sensitive to changes in the ionic composition of water (i.e., being moved from lab water to sample groundwater) (Nautilus *unpublished data*). For example, *Ceriodaphnia dubia* is more sensitive to total dissolved solids than *D. magna*. The approach and biological end points for *D. magna* would be the same as *C. dubia*, however there is no EPA method for a chronic toxicity test using *D. magna*. EPA's Office of Chemical Safety and Pollution Prevention does have test guidance on chronic exposures for *D. magna* and *D. pulex* (EPA 2016). The main difference is the duration of the reproduction test, which would be increased from 7 to 21 days if *D. magna* is used rather than *C. dubia* in the three brood reproduction tests. EPA guidance will be used if the freshwater invertebrate needs to be changed.

8.0 Field Procedures

8.2 Measurement and sampling procedures

Static water levels will be measured in all the monitoring wells upon arriving at the site. Water levels will also be measured during the purging process to ensure that the wells are 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).

Sample order will be based on previous sample results, if available, or professional judgement. Typically wells are sampled from the lowest contaminant concentration to the highest. This helps prevent potential cross-contamination of the sample equipment.

Monitoring wells will be purged and sampled using industry standard low-flow sampling techniques. Wells will be purged at a rate of less than 0.5 L/minute using dedicated tubing at each well. The wells 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.

Once suitable contaminated and control wells are identified for the supply of water for the toxicity tests, we will return and pump 100 L from each well using a submersible pump. Water will be collected into 20 L carboys and shipped in individual coolers to Nautilus Environmental. Once at Nautilus Environmental, all the water will be combined and stored at 4°C in teflon-lined drums for the freshwater and marine toxicity tests.

Prior to beginning the toxicity tests, Nautilus will sample the shipped groundwater to confirm the concentrations of NWPTH-Dx. In addition to samples of the shipped groundwater, Nautilus will submit samples of the laboratory control water for verification that no background contamination exists. This will allow Nautilus to begin the range-finding toxicity tests with a more precise concentration. The dilution series and sampling schedule during the range-finding and final chronic 7-day renewal tests will follow the previous study (Hobbs 2018). The mortality of the organisms will be recorded as both “ecological” mortality, where the anesthetizing properties of the contaminants incapacitate the organism, and absolute mortality of the organism.

During the final toxicity tests additional samples will be taken to allow for characterization of volatile petroleum hydrocarbons and extractable petroleum hydrocarbons (VPH/EPH) of the final NWTPH-Dx effects concentrations. From day 4 to day 7 of the final chronic test, samples will be collected for VPH/EPH, preserved, and stored at Nautilus. Once an effects concentration is evident through mortality of the organisms, the samples collected from suspected NOEC and LOEC dilutions will be analyzed for VPH/EPH. Furthermore, the final effects concentrations of NWTPH-Dx will also be split and run with silica gel cleanup (SGC) as a sample preparation. The hold time of the NWTPH-Dx is 40 days. Therefore, the samples that will be prepared by SGC will be selected once Nautilus has calculated the final effects concentrations based on both mortality and growth end points.

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.

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 preserved
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
Metals‡	water	500 mL HDPE bottle; field filtered	1:1 HNO_3, cool to ≤6°C	6 months
Nitrate-nitrite and ammonia	water	125 mL HDPE	1:1 H_2SO_4, cool to ≤6°C	28 days
Major anions	water	125 mL HDPE	cool to ≤6 °C	28 days
Sulfides	water	500 mL HDPE	2 mL ZnOAc	7 days
Hardness	water	125 mL HDPE	1:1 H_2SO_4, cool to ≤6°C	6 months
Total dissolved solids	water	500 mL HDPE	cool to ≤6°C	7 days
Alkalinity	water	500 mL HDPE	cool to ≤6 °C	14 days
Dissolved organic carbon	water	125 mL HDPE	1:1 H_2SO_4, cool to ≤6°C	14 days

‡ metals includes major cations, priority metals, and mercury.

8.4 Equipment decontamination

Sample equipment used at more than one well, such as an E-tape or submersible pump, will be decontaminated between sample locations. 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.

8.9 Other activities

Purge water from the wells will be stored on-site in 55-gallon drums. This waste will be transported and disposed of in accordance with Washington regulations (WAC 173-340-400).

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	155	500–10,000 µg/L	500 µg/L	SW3535 and SGC*	NWTPH-Dx
NWTPH-Gx	water	7	250–10,000 µg/L	250 µg/L	SW5030B	NWTPH-Gx
BETX‡	water	7	1–1000 µg/L	1.0–2.0 µg/L	SW5030B	SW8021B
Polynuclear aromatic hydrocarbons‡	water	7	0.5–500 µg/L	0.05 µg/L	SW3510C	SW8270DSIM
Volatile petroleum hydrocarbons	water	12	50–500 µg/L	50 µg/L	SW5030B	WA VPH
Extractable petroleum hydrocarbons	water	12	40–5000 µg/L	40 µg/L	SW3510C	WA EPH
Metals (excl. Hg)‡	water	7	0.02–100 µg/L	0.02–1.00 µg/L‡	NA	EPA 200.8
Mercury	water	7	0.05–5.00 µg/L	0.05 µg/L	MEL Hg Prep	EPA 245.1
Hardness	water	7	0.3–200 mg/L	0.3 mg/L	NA	SM2340B
Total dissolved solids	water	7	0.95–5 mg/L	0.95 mg/L	NA	SM2540C
Major cations	water	7	0.025–500 µg/L	0.025 µg/L	EPA 200.7	EPA 200.7
Major anions‡	water	7	0.025–500 µg/L	0.025–0.3 µg/L	NA	EPA 300.0
Nitrate-nitrite	water	7	0.01–100 µg/L	0.01 µg/L	NA	SM4500NO3I
Ammonia	water	7	0.01–2.0 mg/L	0.01 mg/L	NA	SM4500 NH3H
Sulfides	water	7	0.05–2.0 mg/L	0.05 mg/L	NA	SM4500-S2
Dissolved organic carbon	water	7	0.5–5 mg/L	0.5 mg/L	NA	SM5310B

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

*If estimated results below the reporting limit are needed, lab may need to extract using SW3510C; a subset of split samples will also be prepared using silica gel cleanup (SGC) methods.

9.2 Sample preparation methods

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

Nautilus Environmental will be using the same test methods, organisms, and preparation as per the previous study (Hobbs 2018). The sole exception will be that the freshwater invertebrate used in the tests will undergo acclimatization with on-site groundwater. Nautilus uses *Ceriodaphnia* from a brood stock at their facility. Therefore, these organisms are acclimatized to the ionic composition of the water at the facility. For this study to be comparable to the previous study (Hobbs 2018), we will need to use the same brood stock. However, differences in the ionic composition of lab water and sample groundwater can cause an effect response in the organism.

Nautilus will first test the sensitivity of the *Ceriodaphnia dubia* to uncontaminated control water from the site. If there appears to be an impact of this water on the organism, Nautilus will produce two to three generations of *C. dubia* using water from the control groundwater well. These acclimatized *C. dubia* will then be used in the tests with weathered Dx-contaminated water. If we use *C. dubia* acclimatized to on-site control water in the final chronic toxicity test, a positive control test using a spiked reference dose (reference toxicant test) will be completed on this brood of invertebrates.

Should the *Ceriodaphnia dubia* prove to be unable to survive in uncontaminated site water, Nautilus will amend the waters to provide a more suitable ionic composition. If both the approaches to acclimatizing the *C. dubia* fail, Nautilus will switch to using *Daphnia magna* as the freshwater invertebrate, which has a higher tolerance for changes in ionic chemistry (Nautilus, unpublished data).

9.4 Laboratories accredited for methods

To provide comparability and continuity with the previous study (Hobbs 2018), the same labs will be used. Nautilus Environmental in Burnaby, BC, will be conducting the toxicity testing. Ecology’s Manchester Environmental Laboratory will be conducting the water chemistry analysis. Analysis of VPH/EPH will be conducted by an accredited contract laboratory.

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 10. 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
Metals	10% of total samples	1/batch	1/batch	1/batch	1/batch
Anions, cations, nutrients, and sulfides	10% of total samples	1/batch	1/batch	1/batch	1/batch
Hardness, alkalinity, and total dissolved solids	10% of total samples	NA	1/batch	1/batch	NA

Each chronic toxicity test has a reference toxicant control test conducted concurrently. In addition, Nautilus will conduct a control test using the on-site, uncontaminated groundwater. The petroleum hydrocarbon toxicity test end points must be significantly different from the control tests.

15.0 References

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