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Quality Assurance Project Plan

Toxicity Testing of Eastern and Western Washington Soils Contaminated with Gas, Diesel, and Heavy Oil

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Publication Information

Each study conducted by the Washington State Department of Ecology (Ecology) must have an approved Quality Assurance Project Plan. 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.

This Quality Assurance Project Plan is available on Ecology's website at https://fortress.wa.gov/ecy/publications/SummaryPages/1403119.html

Data for this project will be available on Ecology's Environmental Information Management (EIM) website at www.ecy.wa.gov/eim/index.htm. Search Study ID PETROBIO14.

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Quality Assurance Project Plan

Toxicity Testing of Eastern and Western Washington Soils Contaminated with Gas, Diesel, and Heavy Oil

September 2014

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EAP: Environmental Assessment Program
TCP: Toxics Cleanup Program

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Abstract

In Washington, the Model Toxic Control Act (MTCA) is a comprehensive regulatory scheme to protect human health and the environment from contaminated properties. The Washington State Department of Ecology (Ecology) is the lead agency responsible for the implementation and enforcement of MTCA.

Many contaminated sites contain petroleum substances. Petroleum consists of complex mixtures of hundreds of compounds of which petroleum hydrocarbons are one of the principle components. The MTCA classifies petroleum as a regulated hazardous substance.

Procedures for establishing cleanup levels at contaminated sites include testing for Total Petroleum Hydrocarbons (TPH). For soil contamination, the potential impact of TPH on terrestrial ecological receptors must be evaluated and either excluded under justification or a Terrestrial Ecological Evaluation (TEE) must be conducted.

In a TEE, contaminant concentrations are screened, using benchmarks that rely on literature or laboratory analysis on fresh spiked soils rather than the weathered soils more likely to be at contaminated sites. Furthermore, certain petroleum chemicals have no benchmarks assigned. These characteristics of a TEE affect the accuracy and reliability of the results.

The purpose of this study is to collect data for establishing numeric values for ecological screening under the MTCA. This Quality Assurance Project Plan describes procedures to test different levels of plant and soil biota toxicity related to weathered petroleum products of concern. Soil samples will be analyzed for gas, diesel, and heavy oil concentrations and the effects on biota will be quantified using lettuce and earthworm bioassay tests.

Background

Petroleum products originally come from crude oil and consist of complex mixtures of hundreds of compounds. Compounds include various amounts of aliphatic compounds (straight and branched chain, and cyclic alkanes and alkenes) and aromatic compounds (benzene and alkyl benzenes, naphthalenes, and polycyclic aromatic hydrocarbons (PAHs)) (ATSDR, 1999). Many petroleum products contain additives such as alcohols, ethers, metals, and other chemicals that may affect the toxicity of the mixture.

Petroleum hydrocarbons are the principal components in a wide variety of commercial products such as gasoline, diesel, and heavy fuel oils. Because of the widespread use of these products, environmental contamination from petroleum hydrocarbons is relatively common. Assessment of petroleum hydrocarbon-contaminated sites involves analysis for total petroleum hydrocarbons (TPH). TPH represents the total mass of hydrocarbons rather than the identification of individual components and depends on the method of analysis as well as the contaminating material.

When released to the environment, the composition of a petroleum product changes due to weathering (i.e., the breakdown of its components, which causes changes in the component's fate and transport). Hydrocarbons with similar physical and chemical properties are partitioned into fractions. Some fractions migrate to other locations and environmental media, leaving the relatively non-mobile components (the weathered product) at the original location (ATSDR, 1999). The mixtures of concern for TPH are not the heterogeneous petroleum products, but rather the transported fractions to which ecological populations are more likely to be exposed (ATSDR, 1999).

Currently there are limited numeric concentration levels for evaluating ecological impacts of TPH in soils. This study will collect data to support development of appropriate numeric values.

Model Toxic Control Act (MTCA)

The Washington State Department of Ecology (Ecology) is the lead agency responsible for the implementation and enforcement of Model Toxic Control Act (MTCA). The MTCA is a comprehensive regulatory scheme to identify, investigate, and clean up contaminated properties that are, or may be, a threat to human health or the environment. Ecology has issued detailed regulations that supplement the Act. These regulations can be found in Chapter 173-340 WAC (www.ecy.wa.gov/biblio/9406.html). Various policy documents and technical memoranda that help explain how Ecology interprets and applies the MTCA are at www.ecy.wa.gov/programs/tcp/policies/tcppoly.html.

Washington voters approved the MTCA as an initiative in 1988 and the legislature adopted it in 1989 as the counterpart to the federal Superfund law, also known as the Comprehensive Environmental Response, Compensation and Liability Act ("CERCLA"). Unlike CERCLA, the MTCA treats petroleum as a regulated hazardous substance. This is important, because the only

substances of concern at many contaminated sites, such as gas stations and properties with old heating fuel tanks, are petroleum products.

Ecology's Toxics Cleanup Program (TCP) specifies procedures for establishing cleanup levels at sites where there has been a release of petroleum and its associated hazardous substances. Testing for TPH is required for every type of petroleum release. For soil contamination, the potential impact of TPH on terrestrial ecological receptors must be evaluated. Specifically, either exclusion must be established for the site or a Terrestrial Ecological Evaluation (TEE) must be conducted.

Terrestrial Ecological Evaluations (TEE)

An important step in ecological risk assessments for sites that may be contaminated with toxic chemicals is to screen the chemicals for contaminants of potential concern. To determine ecological risk, Ecology uses a TEE for:

- Identifying whether a release of hazardous substances to soil may pose a threat to the terrestrial environment.
- Characterizing existing or potential threats to soil biota and terrestrial plants and animals exposed to hazardous substances in soil.
- Establishing soil concentrations that are protective of soil biota and terrestrial plants and animals.
- Facilitating evaluation of cleanup action alternatives by developing necessary information for a feasibility study.

Part of the TEE screening process entails comparing reported ambient concentrations to a set of toxicological benchmarks. These screening levels (benchmarks) are described in WAC 173-340 in Tables 749-2, 749-3, 749-4, and 749-5 (WAC 173-340, 2007). If the benchmarks are exceeded, they may be used as a conservative cleanup level for the site, or additional, site-specific evaluations may be performed.

Currently, the MTCA lists soil concentration benchmarks for gasoline range organics (GRO) and diesel range organics (DRO) in Table 749-2 (for the simplified terrestrial evaluation) and Table 749-3 (for the site-specific evaluation) but does not list benchmarks for other petroleum products such as heavy oils and mineral oils. Ecology's *Guidance for Remediation of Petroleum Contaminated Sites* directs heavy oils to be summed with DRO and mineral oil considered as essentially non-toxic to plants and animals in (Ecology, 2011b).

Benchmarks for the site-specific evaluation are more conservative and specific for plants, soil biota, and wildlife than the general values listed for the simplified terrestrial evaluation for GRO and DRO. Simplified terrestrial evaluation benchmarks for unrestricted land use include 200 mg/kg for GRO and 460 mg/kg for DRO. In comparison, site-specific benchmark concentrations of 100 mg/kg exist for assessing GRO and 200 mg/kg for DRO in soil biota with respect to toxicity to the soil and litter-dwelling invertebrates, including earthworms, other micro and macro invertebrates, or heterotrophic bacteria and fungi (WAC 173-340, 2007; Ecology, 2011b).

To determine if substances will bioaccumulate to levels that harm animals, wildlife exposure modeling must be conducted. The Wildlife Exposure Model for Site-specific Evaluations uses toxicity reference values based on the logarithm of the octanol-water partition coefficient (log K_{ow}) for obtaining the GRO and DRO wildlife benchmarks, since values for GRO and DRO are not listed in Table 749-5 (Default Values for Selected Hazardous Substances for use with the Wildlife Exposure Model in Table 749-4). Although there are site-specific benchmarks for the protection of wildlife for GRO and DRO (5,000 mg/kg and 6,000 mg/kg respectively), there are none listed for heavy oil (WAC 173-340, 2007; Ecology, 2011b).

These benchmarks are considered protective of soil biota and wildlife. However, it is difficult to translate soil concentrations of chemical releases compared with benchmarks to actual ecological risks for plants, soil biota, or animals. The benchmarks rely on literature survey or laboratory tests using spiked soils[1] or are based on studies of fresh gasoline and diesel products rather than aged (weathered) contamination in soil (Ecology, 2011b; Efroymson et al., 1997a,b). Furthermore benchmark and toxicity reference values are missing for certain petroleum chemicals as stated above.

This study will assess different levels of plant and soil biota toxicity of weathered petroleum products from contaminated soils located within Washington. Categories of petroleum products of concern include gas, diesel, and heavy oil. The sampling and quality assurance (QA) plan described below for this study follows Ecology's guidance for Quality Assurance Project Plans (Lombard and Kirchner, 2004).

Water Resource Inventory Area (WRIA) and 8-digit Hydrologic Unit Code (HUC) numbers for the study area

This study includes screening statewide for potential sample locations.

[1] Clean field-collected or laboratory-created soils are spiked with solutions at different concentrations of the contaminant of interest. The spiked soil is then used to test the toxicity of the contaminant to various organisms.

Project Description

This project is designed to sample contaminated soil known to contain gas, diesel, and heavy oil contamination. TPH-contaminated soils will be evaluated in the field for appropriate use in this project and collected from Eastern and Western Washington sites. Soils will be collected across a gradient of TPH concentrations and fractions. Two toxicity tests will be conducted on each sample to support development of numeric values to evaluate ecological impacts from TPH. Field-collected soils are being used to reflect actual site cleanup conditions.

Each site will be tested for TPH and for defining petroleum fractions within the samples. Soil samples will then be analyzed for toxicity, using lettuce and worm bioassay success. Other measurements to be collected include total organic carbon (TOC), pH, soil characteristics (general field test for grain size, color, type, plasticity, and classification), other elements (metals), and habitat characteristics (general descriptions of landscape and biota).

Study Objectives

The primary objective of this study is to:

- Collect data to support development of ecological screening concentrations for gas, diesel, and heavy oil contamination in weathered soils within Washington for incorporation into the MTCA.

Secondary objectives are to:

- Determine if alternative ecologically relevant benchmarks are practical for use in screening contaminated soils; compare toxicity level concentrations for GRO and DRO from this study to current benchmarks for soil biota.
- Assess bioaccumulation of the petroleum products by determining the bioaccumulation concentration found in earthworm bioassay tests.

Organization and Schedule

Table 1 lists the people involved in this project. All are employees of the Washington State Department of Ecology. Table 2 presents the proposed schedule for this project.

Table 1. Organization of project staff and responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Arthur Buchan Policy and Tech Support Unit, Information and Policy Section, TCP Phone: 360-407-7146	EAP Client	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.
Patti Sandvik Toxic Studies Unit, SCS Phone: 360-407-7198	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.
TBD	Field Assistant	Helps collect samples and records field information. Assists with data analysis and enters data into EIM.
Dale Norton Toxic Studies Unit, SCS Phone: 360-407-6765	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Will Kendra SCS 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.
Brett Muckey CH2M Hill Phone: 541-768-3160 (lab); 541-768-3112 (desk)	Project Manager	Supervises the bioassay testing and ensures accuracy and completeness.
Mark Harris Analytical Resources, Inc. Phone: 206-695-6210	Project Manager	Supervises the VPH and EPH testing and ensures accuracy and completeness.
Joel Bird Manchester Environmental Laboratory Phone: 360-871-8801	Director	Approves the final QAPP. Directs chemists in the analysis of field samples.
William R. Kammin Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP.

EAP: Environmental Assessment Program
EIM: Environmental Information Management database
QAPP: Quality Assurance Project Plan
SCS: Statewide Coordination Section, EAP
TBD: To be determined
TCP: Toxic Cleanup Program

Table 2. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	Due date	Lead staff
Field work completed	10/31/2014	Patti Sandvik
Manchester Laboratory analyses completed	12/31/2014	
Contract Laboratory analyses completed	1/31/2015	
Environmental Information System (EIM) database		
EIM Study ID	ID number: PETROBIO14	
Product	Due date	Lead staff
EIM data loaded	2/28/2015	Patti Sandvik
EIM quality assurance	3/31/2015	TBD
EIM complete	4/30/2015	Patti Sandvik
Final report		
Author lead / Support staff	Patti Sandvik	
Schedule		
Draft due to supervisor	3/31/2015	
Draft due to client/peer reviewer	4/30/2015	
Final (all reviews done) due to publications coordinator	5/31/2015	
Final report due on web	6/30/2015	

Quality Objectives

Quality objectives ensure that data collected during this study are representative of the environment, acceptable for their intended use, and meet the goals and objectives of the project. Representativeness will be achieved by following the study design and procedures detailed in the sections below. Features of the study design and procedures such as sampling location and analysis were developed to reflect the goals and objectives of the study. This QA Project Plan will be taken into the field to ensure the procedures outlined here are followed.

Measurement Quality Objectives

The measurement quality objectives are performance criteria for field measurements and laboratory analyses performed during this study. These objectives specify the techniques and measurements to be performed to assess the precision and bias of the produced results.

Field measurements are expected to adhere to the measurement quality objectives in Table 3. Laboratories are expected to meet the measurement quality objectives outlined in Tables 4 and 5. The lowest concentrations of interest reflect levels below current screening levels for the protection of wildlife and achievable with the specified methods.

Table 3. Soil measurement quality objectives for measurements taken in the field.

Parameters (Units)	Instrument/ Method	Calibration	Standards Check	Range	Accuracy	Resolution
pH	Hach pH meter/ EPA method 9045D	Must be calibrated at a minimum of 2 points that bracket the expected pH values. The temperature of the buffer must be <2°C different from the samples	<±0.1 pH units of buffer solution, check performed prior to sampling, after every 10th sample, and post-sampling	-2.0 to 14.0	±0.01	0.01
Field Conc. Screening (ppm ww)	PetroFLAG®/ EPA method 9074	Before each 10 sample batch or at least daily	Before each 10 sample batch or at least daily	10-10,000*	±10%*†	1 ppm
Various contaminants (e.g., heavy metals)	XRF/ EPA method 6200	Must be standardized with clip or token included with instrument prior to use and after every 4-hour period or as directed by the display	<±20% of standard reference material or soil sample of a known concentration, check performed prior to sampling, after every 20th sample, and post-sampling	>8	±10%	1

Conc.: Concentration.

ww: wet weight.

XRF: X-ray Fluorescence Instrument.

* Linear range analyte dependent.

† From Max Detection Limit (MDL) to Max Linear Range (MLR) ±10% +5 ppm; from MLR to Max Quantifiable Range (MQR) ± 20%.

Table 4. Measurement quality objectives for laboratory chemical analyses.

Analysis (Units)	Lab	Calibration	Method Blank	Laboratory Control Sample[1]	Duplicates	Matrix Spikes	Lowest Conc. of Interest
TOC (%)	MEL	Follow method / instrument specific calibration procedures	≤0.1	-	RSD ≤20%	-	0.1
Total Solids (%)			-	-		-	1.0
NWTPH-Dx (mg/kg dw)	MEL	Methods specified in Ecology, 1997	≤25 - Diesel ≤100 - Oil	50-150%	RPD ≤40%	NA	50
NWTPH-Gx (mg/kg dw)	MEL	Methods specified in Ecology, 1997	≤5	50-150%	RPD ≤50%	NA	5
Fractionated Product Testing using VPH[2] (mg/kg)	ARI	Methods specified in Ecology, 1997	< Lowest PQL	70-130% (Lab fort blk spike)	RPD ±30%	70-130%	5
Fractionated Product Testing using EPH[2] (mg/kg)	ARI	Methods specified in Ecology, 1997	< Lowest PQL	30-160%* (Lab fort blk spike)	RPD ±30%	30-160%*	5

* Variable among analytes.
ARI: Analytical Resources, Inc.
Conc.: Concentration.
dw: Dry weight.
EPH: Extractable Petroleum Hydrocarbons.
MEL: Manchester Environmental Laboratory.
N/A: Not applicable.
NWTPH-Gx: Volatile Petroleum Products (Extended).
NWTPH-Dx: Semi-volatile Petroleum Products (Extended).
CL: Contract Laboratory
PQL: Practical Quantitation Limit
RPD: Relative percent difference.
RSD: Relative standard deviation
TOC: Total Organic Carbon
TPH: Total Petroleum Hydrocarbons
VPH: Volatile Petroleum Hydrocarbons.
1. A known matrix spiked with analytes representative of the target analytes used to document laboratory performance.
2. EPA allows method accuracy for the total of all petroleum hydrocarbons of 70% to 130%.

Table 5. Measurement quality objectives for bioassay tests.

Bioassay Test	Test Conditions				Control Performance
	Temperature	Photoperiod	Soil Moisture Content	Soil pH	
Lettuce	20-30°C	16 hours light 8 hours dark	-	-	Mean germination ≥ 90%
Earthworm	20-24°C	24 hours light	35-45%	5.0-9.0	Survival ≥ 90%

Sampling Process Design (Experimental Design)

In order to address the objectives of this study, a triad approach will be implemented consisting of field assessment, chemical testing, and toxicity testing. Field assessment investigates by observation of the site and estimates whether actual harm appears to have occurred at the site. Chemical testing indicates the presence of contamination and toxicity tests explore whether biological effects are likely. Appendix A includes flowcharts showing the overall sampling design (Figure A-1) and sample screening, collection, and analyses (Figure A-2).

Site Selection

This project is designed to sample contaminated soil known to contain gas, diesel, or heavy oil contamination. A total of 60 samples representing different concentrations of contaminated soils within Washington will be collected. A maximum of five samples at different concentration levels will be collected per site. A minimum of 12 sites will be sampled.

A database search for sites containing gasoline, diesel, and heavy oil contamination in soils will guide sample site selection. Potential locations will be found by searching for reported spills, cleanup sites, and leaking underground storage tanks. Ecology's EIM, Integrated Site Information System (ISIS), internal databases, and professional staff from TCP will help guide the site selection effort. A brief overview of the site selection procedure is described below and a flow chart can be found in Appendix B.

Documents for soil concentrations, background levels, cleanup levels, and bioassay test results of each petroleum product of concern will be reviewed and compiled. Focus will be on finding sites where these types of contamination (i.e., gasoline, diesel, and heavy oil) in soil are known to be present with concentrations above background or cleanup levels. These sites are expected to cause effects detected in the toxicity tests that meet the objective for defining risks to terrestrial plants and animals.

Currently there are thousands of sites listed for historical and current petroleum contamination in soils. To narrow down the selection of sampling locations for this study, sites with petroleum contamination will be further screened for:

- Contaminant status is confirmed above cleanup levels.
- Site type is upland.
- Site status is awaiting cleanup.

Additionally, sites will be screened for homogeneity of each of the petroleum categories to reduce interference with analysis from heterogeneous mixtures of other contaminants. Priority will be given to sites that are listed:

1. Solely for each petroleum category.
2. With three or less other suspicious (not confirmed) contaminants in soil or groundwater, but include no metals, pesticides, radioactive wastes, other deleterious substances, or any other substance that may cause concern for bioassay test interferences.

3. With three or less other suspicious or confirmed contaminants in groundwater but not in soils, but include no substances that may interfere with bioassay tests as listed in number two.

Sites listed for Volunteer Cleanup Program (VCP) will be given serious consideration since these sites likely contain contaminated areas that have weathered petroleum products. To reduce some variability in weathering, sites less than five years old will be given priority.

After searching and filtering Ecology's large databases (e.g., EIM, ISIS, and other internal databases), we will compile the results and sort for individual site information including background and cleanup levels. We will collect documents for the potential sample sites. We will retain a number of sites for each petroleum type and area in order to have alternate locations in case screening assessments determine the soils do not meet the conditions for positive results in bioassay tests. See discussion below in Assessment and Analyses section.

Final site selection will include half of the locations from each of the east and west sides of the Cascades Mountain Range to represent different soils statewide.

Petroleum Types

Table 6 lists categories and carbon ranges for the petroleum products of concern for this study (adapted from Ecology, 2011b). These products are the same as those listed in Table 830-1 of the MTCA.

Table 6. Categories of petroleum products and their approximate (~) carbon range.

Categories	Gasoline	Middle Distillates/Oils	Heavy Fuels/Oils
	GRO ~ C5-C13	DRO ~ C8-C21	DRO ~ C12-C34
Products	Automotive Gasoline	Diesel No. 1	Bunker C
	Aviation Gasoline	Kerosene	No. 4 Fuel Oil
	Automotive Racing Fuels	Diesel No. 2	No. 5 Fuel Oil
	Mineral Spirits	Diesel & Biodiesel mixtures	No. 6 Fuel Oil
	Naphtha	Home heating oil	Products included under waste oil before use
	Stoddard Solvents	Jet Fuel (e.g., JP-4, JP-5, JP-7, JP-8)	
		Light Oil	

DRO: Diesel Range Organics.
GRO: Gasoline Range Organics.

Each of the three petroleum categories of interest will be sampled on each side of the mountains: gasoline, diesel (middle distillates), and heavy oil. Waste oil will not be included in this study as it generally contains other toxics that would bias the results. Alternate sample sites will be identified for each area and for each petroleum type.

Petroleum Concentration Ranges

During site selection, we will compile data on the soil concentration of the different petroleum products along with background and cleanup levels to evaluate the soils at the site. Whole product analysis using Northwest TPH -Gx (NWTPH-Gx) and Northwest TPH -Dx (NWTPH-Dx) methods will be used to verify the concentration of gasoline range compounds (Gx) or diesel and oil range compounds (Dx) present at the site.

To establish general guidelines of effective concentrations for each petroleum category of interest for this study, a literature search was conducted. Overall, little information was found confirming levels for lethal effects. However, one of the most comprehensive summaries for effective concentrations was conducted by the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) in Canada. The TPHCWG reviewed scientific, technical, and economic analysis to reduce information gaps and uncertainties for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil (PHC CWS) (CCME, 2008). In Canada, PHC are considered in four broad physico-chemical fractions synthesized from the sub-fractions defined by the US Total Petroleum Hydrocarbons Criteria Working Group. The fractions are defined in equivalent carbon numbers as follows:

F1: C6 to C10
F2: >C10 to C16
F3: >C16 to C34
F4: C34+

Aliphatic and aromatic sub-fractions are handled separately in the human health assessment.

Figure 1 compares Ecology's and Canada's PHC categories for regulatory use.

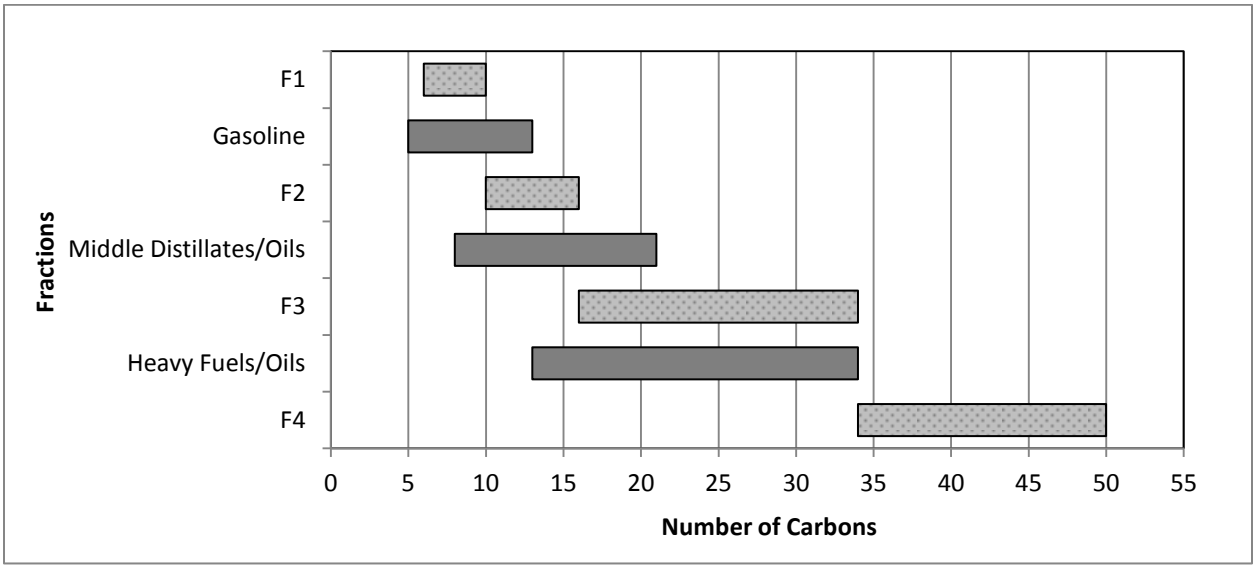

Figure 1. Carbon range comparisons between Ecology's and Canada's petroleum categories for regulatory use.

Gasoline, Middle and Heavy Fuel Oils categories are used by Ecology, whereas F1 to F4 are for Canada.

Multiple studies were compiled during the TPHCWG review to compare effects between petroleum fractions and concentrations. Table 7 summarizes a range of lethal effective soil concentrations on plant and biota taken from the technical report created from this extensive review (CCME, 2008). To adjust for the differences between Canada and Ecology's fraction categories, some interpolation was necessary.

Table 7. Estimated ranges of soil concentrations showing lethal effects on plant and soil biota (mg/kg).

Petroleum Product Type	F1	F2	F3 (fine soil)	F3 (coarse soil)	F4
Gasoline	400-9,620	530-8,240			
Middle Distillates/Oils			924-84,261	5,969-86,548	
Heavy Fuels/Oils					
Crude Oil (or above C34)					16,696-100,000

Fractions 1-4 are PHC CWS: Canada-Wide Standard for Petroleum Hydrocarbons in Soil (CCME, 2008).
Gasoline, Middle Distillates, and Heavy Fuels/Oils are Ecology's categories for Table 830-1 in the MTCA.

Although TPHCWG reports results for F4 fraction, this study is not testing for petroleum fractions above C34. Furthermore, these values are not cleanup values, but they can provide comparison values to help determine if the site has contamination levels high enough to affect organisms in the bioassay tests.

Since the range of these categories is large and no guidelines are given for effective concentrations to be used in bioassays assessing petroleum products, this study will target a range of soil concentrations that span each range listed above. Attempts will be made to collect at least some soil samples that contain the upper end of the range to assure lethal effects in the bioassays. For the Gasoline and Middle Distillates/Oils categories, soil samples with concentrations above 9,620 mg/kg should be collected along with soil samples with decreasing concentrations. Similarly, soil samples with concentrations as high as 87,000 mg/kg may be necessary to show lethal effects for the Heavy Fuel/Oils category, but samples with decreasing concentrations will also be collected.

Most of these concentrations will be well above the screening levels for a TEE. Some screening levels for industrial or commercial properties are higher, but these are excluded in the TEE except when protecting endangered species or when they must comply with local government land use.

Assessment and Analyses

Field Assessment

Each site will be assessed for potential use as a sample location. A field assessment will be conducted making use of all the information available about the site and its contaminant history. Historical information will be compared and verified with the current observation. During the assessment, evidence of any contamination impacts will be noted for possible sample points at that site that may contain the level of contaminant concentration needed to show biological effects in the bioassay tests. Such evidence include petroleum stains (smears) on soil, oil slicks, petroleum odor, lack or stunted vegetation or low animal abundance compared to nearby areas, and barriers or signage designating contaminated areas.

Results from the field assessments may not clearly show contaminated areas. Furthermore, adverse ecological effects might not be demonstrated. Professional judgment will be required to make a decision regarding sample sites and more specifically, sample points within each site.

To help screen for targeted concentrations levels at a sample point, a subsample will be tested using a PetroFLAG® field test kit for TPHs in soil. PetroFLAG® quantifies fuels, oils, and greases as total hydrocarbons but does not distinguish between aromatic and aliphatic hydrocarbons (Dexsil, 2014; EPA, 2007a). Quantifiable ranges using PetroFLAG® standard reagents include 10 to 10,000 ppm ww and up to 200,000 ppm ww using high range reagents. Hydrocarbon determination relies on historical information for the site and is confirmed with laboratory analyses as described below.

Subsamples will be tested for other elements (e.g., metals) using an X-ray Fluorescence Instrument (XRF). The XRF is able to identify and provide relative amounts of elements present in samples by measuring the unique fluorescent x-rays emitted by the different elements. This ancillary information will provide a database that will help define the samples along with pH and TOC.

Other general observations will be noted during the field assessment such as local environmental and wildlife conditions, anthropogenic activities, and current climate conditions. These may be useful in interpreting results.

Chemical Testing

Samples will be screened initially by product type and concentration using the PetroFLAG® field test kit as mentioned above. Those sites where screening samples meet the necessary TPH concentrations will be further sampled for laboratory and bioassay analyses. Samples will be confirmed with laboratory analyses, using the NWTPH-Gx and NWTPH-Dx for gasoline, diesel, and oil range respectively as discussed above and diagramed in Appendix A-2. Hydrocarbon results from the field and laboratories will be compared on a dry weight basis.

Soil samples selected for the lettuce and earthworm bioassay tests will be analyzed for 12 subgroups or "equivalent carbon (EC) fractions" of TPH using the volatile petroleum hydrocarbons (VPH) and extractable petroleum hydrocarbons (EPH) methods in order to confirm the category of the petroleum product in the samples. The VPH method identifies volatile hydrocarbon fractions and the EPH identifies semi-volatile and non-volatile hydrocarbon fractions. These analyses will determine the concentration of aliphatic and aromatic hydrocarbons in specific carbon ranges (fractions). Some EC fractions will have results from both methods in samples analyzed for VPH and EPH. Table 8 shows the EC fraction overlaps (adopted from Ecology, 2011b). When overlap occurs, the highest value will be used in accordance with the Guidance for Remediation of Petroleum Contaminated Sites (Ecology, 2011b).

Table 8. Equivalent Carbon (EC) fraction overlaps between VPH and EPH Methods.

VPH Method	EPH Method
Aliphatic EC 5-6	
Aliphatic EC>6-8	
Aliphatic EC>8-10	**Aliphatic EC>8-10**
Aliphatic EC>10-12	**Aliphatic EC>10-12**
	Aliphatic EC>12-16
	Aliphatic EC>16-21
	Aliphatic EC>21-34
Aromatic EC>8-10	
Aromatic EC>10-12	**Aromatic EC>10-12**
Aromatic EC>12-13	**Aromatic EC>12-13**
	Aromatic EC>16-21
	Aromatic EC>21-34

Bold: points of overlap.

In addition to the petroleum tests described above, soils will be analyzed for total organic carbon (TOC) and reported on a dry weight basis. Dry weight (solids) is measured as a percentage of the wet weight in each sample. Organic matter in the soil is important in reactions of many contaminants in the soil. Organic and inorganic soil constituents contain negatively charged sites that interact with positively charged ions in soil solution. These interactions partially control the effective toxicity of many contaminants (Efroymson et al., 1997a,b). To reduce variability among soil samples, high or low organic soils will be avoided. This will be determined during the field assessment of soil characteristics as discussed below.

Toxicity Testing

Soil samples will be evaluated for toxicity, using lettuce and earthworm bioassays, once the sites are verified to have contaminants that are expected to cause effects detectable by the bioassay tests. Lettuce (*Lactuca sativa*) and earthworms (*Eisenia foetida*) are standard test organisms, widely available, sensitive to the test material, and representative of vital components of ecological landscapes and soil fauna (Efroymson et al., 1997a,b; ASTM, 2009a, 2012; Norton, 1996a,b).

The bioassays will be conducted to identify a toxicity threshold by testing multiple samples at varied concentrations of contamination. Site soils will be collected with a range of contamination to create a series of concentrations. These are abbreviated static acute tests that expose the test organisms to a broad range of media concentrations for 14 days. The acute toxicity tests are short-term tests that measure the effects of exposure to concentrations of chemicals. Static tests are tests that use the same sample medium throughout the duration of the test.

Limitations for static tests include depletion of nutrients, possible breakdown of the contaminants, and the release of metabolites from the organisms (e.g., waste substances), which could affect the accuracy of the medium's toxicity. The short duration of the tests (i.e., 14 days) should reduce the effects of these limitations and, essentially, the limitations will be assessed through the use of a control.

The measurement endpoint reflects the extent of lethality. This study will measure the LC_{50} median lethal concentration, which is the concentration at which 50% of the organisms died. Since the results are estimates of the effects from specific concentrations of contaminants, statistical coefficients of variation can be calculated for them (EPA, 1994). Test data are analyzed using regression models that assume the more concentrated the sample, the greater will be the effects.

Contaminant concentration in the earthworm tissue will be analyzed after a 28-day exposure to soil sample to assess bioaccumulation. The bioaccumulation tests will be conducted on soil concentrations below the lethal concentrations ($LC_{50)}$ found in the 14-day toxicity tests. The soil samples used for the bioaccumulation tests will be chosen according to an appropriate concentration ($<LC_{50}$) determined from the shorter toxicity tests. The magnitude of contaminant concentration is determined from the earthworm tissue concentration above the concentration in the negative control soil.

Sampling Procedures

We will assess, characterize, and chose sample points for each chosen potential site (see description below). We will collect a soil sample to verify that the concentration of the petroleum product is high enough to test for effects on lettuce and earthworms used in the bioassay tests. The site should match historical documents for that site obtained during the site selection process, and the soil concentrations must be elevated (above background and cleanup levels). We will collect a range of soil concentrations to test different levels of toxicity to plants and biota.

Site Assessment

Site terrain and contaminant history will be carefully studied in order to place sampling points in areas that most likely will contain the highest range of concentrations of the chemical of concern (e.g., gasoline, diesel, and heavy oil).

We will assess sites by using historical documents and possibly a pre-sampling site visit to verify information. Documents may characterize the site by habitat information, soil type, physical or chemical soil tests, and detailed description of the area of contamination. A general description of the flora and landscape type will be recorded during the visit. Wildlife or any signs of wildlife (e.g., scat, prints, and hairs) present at the site will be noted. Soil biota will be assessed for presence and general abundance of beetles or other macroinvertebrates and earthworms. Recent soil disturbances, especially evidences of plowing, construction, or other anthropogenic activities that may influence sampling will be recorded. Weather, temperature, general wind speed, cloudiness, and precipitation will be noted during sampling.

A small surface soil sample will be collected in the area of interest. This sample will be used for screening one or more criteria in the field by assessing for total hydrocarbons using PetroFLAG® field test kit for TPHs in soil, pH, and some soil characterization such as color and type (Appendix C). If the location is not appropriate (does not fit screening criteria discussed above in Sample Process Design), we may use another location. Once we confirm the area, we will mark the sampling area with a stake or other marking as appropriate and record with a global positioning system (GPS). We will use this information to return to the same location for additional samples if needed and to map with Geographic Information System Software (GIS).

Soil Collection

Soil samples will be collected from areas of the site expected to have the highest concentration of the petroleum product of concern. For each site, we will obtain up to five samples with increasing concentrations. This will create a series of concentrations to be used for toxicity testing and minimize the potential for result values to be below the reporting limit.

We will collect and test soil in the field, using the PetroFLAG® field tester. If PetroFLAG® results show concentrations within the targeted range (Table 7) then we will retain samples and send to the laboratory for NWTPH-Gx, NWTPH-Dx, VPH, and EPH analyses to confirm the

product type and to verify elevated contaminant concentration. Alternate sites will be sampled if the original site has low contaminant concentrations (below minimum concentration for bioassay tests as described above).

If the NWTPH-Gx and NWTPH-Dx tests give positive results, the investigator reviews the chemical data and contaminant history for the site before making the serious commitment of resources for the other analyses. Bioassay testing will precede once the product and appropriate concentration has been determined for all sites. Scheduling for sample collection and prompt analysis will be coordinated with the laboratories so holding times are not compromised.

Soil samples will be collected using a soil auger, a stainless steel shovel or hand trowel, or stainless steel spoon and will be placed in a stainless steel bowl. Non-soil components such as roots, twigs, and large rocks may be removed by hand and noted on field logs. No sieving is planned except for a soil identification sub-portion. If samples are collected in parts, due to difficult environment, then those samples will be homogenized in a stainless steel bowl with a stainless steel spoon. Once homogenized, subsamples will be taken for chemical analyses, TOC, pH, XRF analysis, soil assessment, and bioassays.

After we transport subsamples back to Ecology's Operation Center, we will air-dry and separate them, using number 200, 40, and 4 sieves for categorizing the soil (ASTM, 2009b). Grain size will then be determined from the soil assessment subsamples. Grain size will be estimated by dry weight as % coarse (mass retained in #4 sieve), % sand (mass retained in #40 and #200 sieve), and % fine material (mass passing through #200 sieve).

At Ecology, we will conduct ancillary element identification and estimated concentrations using an XRF on the sub soil samples used for grain size.

For VPH and EPH analysis, we will take subsamples, using specially designed sealed-tube devices that obtain an airtight soil sample and extruding directly into the soil. These devices are commercially available or provided by the laboratory doing the analysis. Samples for volatile organic compounds (VOC) will be preserved as directed by Ecology's or the analyzing laboratory's instructions (Ecology, 2004a,b, 2008). These samples will be cooled immediately on ice and transported to the analyzing laboratory within 48 hours.

After the initial bioassays are completed and results indicate which samples have appropriate low concentration to sustain earthworms for the 28-day duration, additional samples will be collected for the bioaccumulation tests. Each of these samples will undergo the same procedure and TPH analyses as above, but without additional VPH or EPH analyses.

All sampling equipment (soil auger, hand trowel, spoons, and collection bowls) will be cleaned before use at each site. The cleaning process will follow the Standard Operating Procedure (SOP) for decontaminating sampling equipment (Friese, 2014) and includes washing with water and phosphate-free detergent, rinsing with distilled water, pesticide-grade acetone, and then hexane.

Sample Labeling, Storage, and Handling

All sample containers will be labeled with the site name, date and time of collection, sample matrix, MEL sample ID, and analysis to be performed. Two field replicates will be collected for the bioassays during the study and labeled in a similar manner for use as quality control samples.

After collection, all samples will be stored on ice and transported to Ecology storage facilities. All samples will be held at <4 (±2) °C or frozen at (-18 to -20 °C), depending on the analysis storage condition requirements and when testing will occur.

Table 9 shows recommended containers, storage conditions, and holding times for the analyses that will be performed.

Table 9. Sampling containers, preservation method, and holding times.

Analysis	Laboratory	Container Size	Container Material	Storage Conditions	Holding Time	Dry Mass Required
Chemistry						
Field Conc. Screening	N/A	Dexsil test kit supplies and specifies apparatus and materials		4-45°C	<20 min.	10 g
Grain size and elements	NA	8 oz	Plastic jar	0-6°C	6 months	100 g
pH	N/A	4 oz	Glass with Teflon lined screw cap	Ambient	<1 day	20 g
TOC	MEL	2 oz		0-6°C	14 days	25 g
				≤-18°C	6 months	
NWTPH-Dx		8 oz		0-6°C	14 days	250 g
NWTPH-Gx		4 oz w/Septum		0-6°C	14 days	250 g
EPH	ARI	4 oz	Wide mouth amber glass with Teflon-lined screw cap	0-4°C	7 days	2 x 120 mL
VPH	ARI	40 mL	VOA vials with PTFE-lined septa	0-4°C	14 days	2 - VOA 40 mL vials + 10g
Bioassays						
Lettuce[1]	CH2M Hill	3 liters (3 x 1 liter)	Glass	Cool to ≤6°C	14 days	0.5 L
Earthworm[1]						0.75 L
Bioaccumulation[2]	CH2M Hill	12 liters (~3 gallons)	Plastic buckets (lined) and inserted in metal buckets	Cool to ≤6°C	14 days	10-12 L

[1] 14-day toxicity test. Collecting two times enough soil for reserve.
[2] 28-day earthworm test. Collecting two times enough soil for reserve.
Conc. : Concentration.
MEL: Manchester Environmental Laboratory.
N/A: Not applicable.
NWTPH-Gx: Volatile Petroleum Products (Extended).
NWTPH-Dx: Semi-volatile Petroleum Products (Extended).
TOC: Total Organic Carbon.

Decontamination

All equipment used to collect samples will be stainless steel or Teflon-coated and will be cleaned before use at each site following Ecology's SOP for Decontaminating Field Equipment for Sampling Toxics in the Environment (Friese, 2014) as follows:

- Washed with phosphate-free Liquinox® detergent.
- Rinsed with tap water and then with distilled water.
- Rinsed with acetone.
- Rinsed with hexane.
- Allowed to air dry.
- If not used immediately, wrapped in aluminum foil.

Methanol rinse will not be used, since low level sampling (near the reporting limits) is not anticipated.

Sampling equipment, such as augers, trowels, spoons, and sieves, used at multiple sites will be fully cleaned prior to use at the next location. Nitrile powder- free gloves will be worn while collecting samples to further prevent contamination between sites.

To prevent the spread of invasive species, staff will follow procedures outlined in the Standard Operating Procedure (SOP) document for Minimizing the Spread of Invasive Species (Ecology, 2012a). All field gear will be visually inspected for dirt, seeds, vertebrates, and vegetation. These will be brushed or washed off at the site before moving to the next site. Field personnel will follow this same process for their shoes and clothing.

Waste Management

All excess soil and rinse water will be returned to the sampling location. Solvent rinsate and pH standards will be collected and disposed of at Ecology according to Ecology's chemical hygiene plan. Disposable materials produced in the field such as gloves and paper towels will be collected in garbage bags and removed from the study site for proper disposal in a waste receptacle.

Safety

Sites will be evaluated to determine if they require specialized training to access the site (e.g., Hazardous Waste Operations and Emergency Response (Hazwoper) training) and the level of personal protection needed for safety. Trained personnel will be used for field collection in sites where such safety concerns exist. All other sites will follow the safety procedures discussed below.

Safety protocols found in the latest version of Ecology's Chemical Hygiene Plan and the Environmental Assessment Program's Safety Manual (Ecology, 2011a, 2012b) will be followed when in the field and laboratory. Gloves will be worn when handling samples to prevent cross

contamination with any contaminants. Staff will stay up-wind of soils disturbed during sampling when soil particles are likely to become air-borne, e.g., in dry and windy conditions. Dust masks and safety goggles may be used in the field to prevent inhalation or protect eyes. As an added precaution, all sources of ignition will be kept away from petroleum-contaminated samples.

The XRF will only be operated by staff who have received training for *Level one Radiation Safety Training for XRF Operation.* Other staff present while the XRF is in use will follow the instructions of the operator to prevent accidental exposure to radiation.

All directions from staff, escort, and signage will be followed.

Chain of Custody

Chain of Custody (COC) is a procedure meant to ensure that samples are handled, stored, and transported appropriately and no evidence of sample tampering exists. Its purpose is to trace sample possession from the time of collection through analysis, ensuring creditability to results. When samples are collected, the date and time of collection and a sample ID will be recorded on the container and in the field notes. Once the samples arrive at Ecology, they will be inventoried and a standard chain of custody form will be filled out. Custody of the samples will be transferred and documented on a COC form to a parcel shipping firm (if sent to a contract laboratory), to analytical laboratory staff, and to couriers. A copy of the completed form will be returned to the project manager to keep in the project files.

Shipping

Soil samples to be analyzed or tested by CH2M Hill Applied Sciences Laboratory will be expedited in a cooler with packing material (e.g., bubble wrap) and bottled ice. They will then be sealed for tamper monitoring via a courier. Subsoil to be analyzed by MEL will be shipped in coolers with ice via an Ecology courier. Subsoil samples to be analyzed or tested by Analytical Resources, Inc. will either be shipped on ice with a tracking number to track progress or will be couriered by Ecology staff. Upon receipt, MEL and contract lab staff will record the temperature, inventory the samples, and note other observations on the Chain of Custody form.

Measurement Procedures

Table 10 shows the methods and reporting limits for analysis of soil samples. Soil texture determinations will be made by following the Soil Characteristics directions found in Appendix C. Soil types will be characterized by observation in the field for coarse versus fine grain, but determined volumetrically back at Ecology's Operation Center on dry soil (<3 inch, 75 mm). Grain size will be based on a series of sieves (0.075 mm (No. 200), 4.75 mm (No. 4), and No. 40). Soil color will be determined using basic color scheme as described in the Soil Characterization protocol.

Table 10. Methods and reporting limits for measurements and analyses.

Analysis	Instrument/ Technique	Analytical Method	Reporting Limit/ Resolution
Field Measurements			
pH	Orion pH meter	EPA method 9045D	0.1
Field Conc. Screening	PetroFLAG	EPA method 9074	200* - Gas 13 - Diesel 18 - Oil ppm ww
Various Contaminants (e.g., metals)	XRF	EPA method 6200 & Instrument Manual	10 ppm†
Laboratory Measurements			
TOC	-	PSEP, 1997	0.10%
Total Solids	-	SM 2540G	1%
Semi-volatile Petroleum Products (diesel and heavy oils)	GC/FID	NWTPH-Dx Ecology, 1997	25 - Diesel 100 - Oil mg/kg dw
Volatile Petroleum Products (gasoline)	GC/FID	NWTPH-Gx Ecology, 1997	5 mg/kg dw
Fractionated Product Testing using VPH	GC/FID	VPH Ecology, 1997	5 mg/kg dw
Fractionated Product Testing using EPH	GC/FID	EPH Ecology, 1997	5 mg/kg dw

*Due to the non-linear response curve of Gasoline, quantification below 1000 ppm may underestimate the true contamination.
†Analyte dependent.
Conc. : Concentration.
dw: dry weight.
EPH: Extractable Petroleum Hydrocarbons.
GC/FID: gas chromatography/flame ionization detection.
N/A: Not applicable.

NWTPH-Gx: Volatile Petroleum Products (Extended).
Notes for Table 10 continued:
NWTPH-Dx: Semi-volatile Petroleum Products (Extended).
PSEP: Puget Sound Estuary Program.
TOC: Total Organic Carbon.
TPH: Total Petroleum Hydrocarbons.
VPH: Volatile Petroleum Hydrocarbons.
XRF: X-ray Fluorescence Instrument.
ww: wet weight.

Hydrocarbons will be screened in the field using PetroFLAG® analysis. PetroFLAG is a broad spectrum field analytical tool that uses a unique (patented) system of extractions, analytical reagents and a hand-held battery-powered analyzer to read contamination levels directly in parts per million (ug/g). The test is performed using three steps: extraction, filtration, and analysis.

Hydrocarbon results from the field and laboratories will be compared on a dry weight basis. Percent moisture determination is included in the bioassay analyses. Samples with up to approximately 15% water by weight will be converted to dry weight from PetroFLAG® wet weight results using:

R'=R((2/FS) - 1)

where:
R' = "Dry Weight" Corrected Result
R = Result displayed by PetroFLAG unit
FS = Fraction Solids
where:
FS = (100 - %water)/100

Outside this range or in heavier clay soils, the effect of water content will vary with the analyte and will be evaluated specifically for each site.

Table 11 shows the measured end points for each bioassay tests conducted.

Table 11. Laboratory procedures for bioassay analyses.

Bioassay	Endpoints Measured	Methods
Lettuce	Survival, Biomass	Norton, 1996a, ASTM E 1963-09 (2009a)
Earthworm	Survival, Concentration	Norton, 1996b, ASTM E 1676-12 (2012), EPA 600/3-88/029 (1988)

Concentration levels for survival at which 50% of the organisms died (LC_{50}) support development of ecological screening concentrations for gas, diesel, and heavy oil contamination in weathered soils within Washington for incorporation into the MTCA. Test data are analyzed using regression models (coefficients of variation). These results will be used to compare toxicity level concentrations for GRO and DRO from this study to current benchmarks for soil biota.

Bioaccumulation for earthworms will be measured following the methodology described above (Table 11) using a simple comparison of worm concentration to soil concentration to obtain the ratio of uptake at apparent steady state or bioaccumulation factor (BAF). The BAF will be used for the wildlife exposure model and the predatory receptors of shrew and robin.

Quality Control Procedures

Quality control measures required in this plan will help reduce or explain some of the variability found in this study (Table 12). These were designed to evaluate adherence to the measurement quality objectives developed to support the goal of this study in the use of the measured concentration to understand toxicity rather than to characterize contaminant concentration. Protocols for sampling and analyses will be followed according to directives: MEL's Laboratory User's Manual and Quality Assurance Manuals (MEL, 2008, 2012), contract laboratory manuals, SOPs, and professional judgment and experience.

Table 12. Frequency of quality control procedures.

Analysis	Field Replicates	Method Blank	LCS	Analytical Duplicate	Matrix Spike
Field Measurements					
pH	1/10 samples	-	-	-	-
Field Conc. Screening	1/10 samples	1/10 samples	-	-	-
XRF	1/10 samples	-	1/day	-	1/day
Laboratory Measurements					
TOC	1/30 samples	-	-	1/batch	-
% Solids	1/30 samples	-	-	1/batch	-
NWTPH-Dx	1/30 samples	1/20 samples	1/20 samples	1/10 samples	-
NWTPH-Gx	1/30 samples	1/20 samples	1/20 samples	1/10 samples	-
VPH	1/30 samples	1/20 samples	1/20 samples	1/20 samples	1/20 samples
EPH	1/30 samples	1/20 samples	1/20 samples	1/20 samples	1/20 samples
Bioassays	1/30 samples	-	-	1/60 samples	-

EPH: Extractable Petroleum Hydrocarbons.
N/A: Not applicable.
NWTPH-Gx: Volatile Petroleum Products (Extended).
NWTPH-Dx: Semi-volatile Petroleum Products (Extended).
TOC: Total Organic Carbon
TPH: Total Petroleum Hydrocarbons
VPH: Volatile Petroleum Hydrocarbons.
XRF: X-ray Fluorescence Instrument.

Possible source of bias may exist because of some inherent limitations within this study. Limited resources determined the number of soil samples and analysis to be performed, which may introduce bias for interpolating results for a larger area or population. Although the direction and magnitude of these potential biases are unknown, samples and analyses were chosen for the most efficient and effective results.

The budget for this study is shown in Table 13.

Table 13. Budget for this study.

Analysis	Samples (#)	QC[1]	Cost/Sample ($)	Total ($)
Manchester Environmental Laboratory				
TOC	65	4	$46.00	$3,174.00
Percent Solids[2]	65	3	$0.00	$0.00
NWTPH-Dx	65	4	$75.00	$5,175.00
NWTPH-Gx	65	4	$60.00	$4,140.00
Lipids (worm tissue)	3	1	$33.00	$132.00
CL: Analytical Resources, Incorporated				
VPH	62	3	$125.00	$7,750.00
EPH	62	3	$130.00	$8,060.00
CL: CH2M Applied Sciences Laboratory				
Lettuce - 14 day	62	1	$550.00	$34,650.00
Earthworm - 14 day	62	1	$550.00	$34,650.00
Earthworm - 28 day	3		$1,800.00	$5,400.00
Equipment / Miscellaneous				
pH Probe and Buffers				$500.00
Other				$5,000.00
Project Total				
				$108,631.00

1. 1/20 samples field replicate, lab duplicate, matrix spike, and standard reference material analyses.
2. Percent Solids values are included in NWTPH-Dx and -Gx analysis.
CL= contract lab.
EPH=Extractable Petroleum Hydrocarbons.
NWTPH-Dx=Northwest TPH hydrocarbon-Dx (extended).
NWTPH-Gx=Northwest TPH hydrocarbon-Gx (extended).
QC=quality control.
TOC=Total Organic Carbon.
VPH=Volatile Petroleum Hydrocarbons.

Data Management Procedures

Data management is a large and critical part of this study. The project manager must keep careful record of each step of the process by documenting or collecting documents for:

- Sampling plans.
- Laboratory contracts.
- Field sampling log.
- Sample chain of custody and management.
- Laboratory results.
- Quality control sampling and results.

Field data and observations will be recorded in notebooks on waterproof paper. The information contained in field notebooks will be transferred to Excel spreadsheets (Microsoft 2007) after returning from the field. Data entries will be independently verified for accuracy by another member of the project team.

The data package from MEL will include a case narrative discussing any problems encountered in the analyses, corrective actions taken, changes to the requested analytical method, and an explanation of data qualifiers. Laboratory quality-control results will also be included in the data package. This will include results for surrogate recoveries, laboratory duplicates, matrix spikes, check standards/laboratory control samples (LCS) blanks, and ongoing precision and accuracy (ORP) standards/labeled compounds included in the sample batch. The information will be used to evaluate data quality, determine if the MQOs were met, and act as acceptance criteria for project data.

Data from the analyzing contract laboratory will be submitted in electronic or printed format per contract. MEL will give a complete data package, as described above, to the project manager after it completes a quality-control review for those laboratories contracted by them. The project manager will conduct a final review of data packages.

Results from the project will be published in a report. Laboratory data will be entered into Ecology's EIM database. Data entered into EIM will follow a formal data review procedure where data are reviewed by the project manager of the study, the person entering the data, and an independent reviewer.

Audits and Reports

Audits

MEL participates in performance and system audits of their routine procedures. Results of these audits are available on request. The VPH and EPH analyses as well as the bioassay tests are contracted out to laboratories accredited by Ecology for those methods. The Environmental Laboratory Accreditation Program evaluates a laboratory's quality system, staff, facilities and equipment, test methods, records, and reports and establishes that the laboratory has the capability to provide accurate, defensible data. Results of on-site assessments and proficiency tests are available from Ecology on request.

Reports

The project manager for this study will prepare a draft report, summarizing the results of this study, for review by the client and other interested parties. The final report will be prepared by the end of March 2015.

The final report will include:

- Maps of the study area showing sample locations.
- Coordinates and detailed descriptions of each site.
- Descriptions of field and laboratory methods.
- Discussions of data quality and the significance of any problems encountered in the analyses.
- Summary tables of the chemical and ancillary data.
- Assessment of the toxicity levels pertaining to each location where bioassays were performed.
- Comparison of the current TEE screening levels to the toxic concentration level found in this study.
- Bioaccumulation factor found in the earthworm bioassay tests.
- Evaluation of the use of study results to represent TEE screening levels in other locations within Washington.
- Recommendations resulting from this study.

Project data will be entered into Ecology's EIM system. Public access to electronic versions of the data and reports generated from this project will be available via Ecology's internet homepage (www.ecy.wa.gov).

Data Verification and Validation

Data Verification

Analytical Resources, Inc. and CH2M Hill Applied Sciences Laboratory (contract laboratories) will provide documentation describing the method and QC procedures used on project samples. Any problems encountered with analysis will be described for each sample. A copy of the chain-of-custody form will be returned to the project manager along with any other documentation supporting the verification of the results.

MEL will conduct a review of all laboratory data and case narratives contracted through them. Contracts initiated outside of MEL will be reviewed by the project manager. Verification will show that:

1. Methods and protocols specified in the QA Project Plan were followed.
2. All calibrations, checks on quality control, and intermediate calculations were performed for all samples.
3. Data are consistent, correct, and complete, with no errors or omissions.

Evaluation criteria will include the acceptability of holding times, instrument calibration, procedural blanks, spike sample analyses, precision data, laboratory control sample analyses, and appropriateness of data qualifiers assigned. MEL will prepare written data verification reports based on the results of their data review. A case summary will meet the requirements for a data verification report.

To determine if project MQOs have been met, the project manager will compare results on field and laboratory quality-control samples to the MQOs. To evaluate whether the targets for reporting limits have been met, the results will be examined for non-detects and to determine if any values exceed the lowest concentration of interest.

The project manager will also review the laboratory data packages and Manchester's data verification reports. The project manager will work with MEL and the contract laboratories to address any concerns with the data, such as errors or omissions. Based on these assessments, the data will be either accepted, accepted with appropriate qualifications, or rejected and re-analysis considered. Data verification will be documented in the annual progress reports.

Data Validation

Extra validation is not proposed for this study.

Data Quality (Usability) Assessment

Once the data have been verified, the project manager will determine if the data can be used to make the calculations, determinations, and decisions for which the project was conducted. Data will be used to evaluate toxicity levels of petroleum products in soil and their risks to terrestrial plants and animals. Statistical analyses will be used when warranted; however, due to the limited number of samples collected in this study, general comparisons, simple statistics, and graphical representations of the data may be more appropriate. Conclusions from these analyses will address the objectives of the study.

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Appendices

Appendix A. Sample Plan Flow Charts

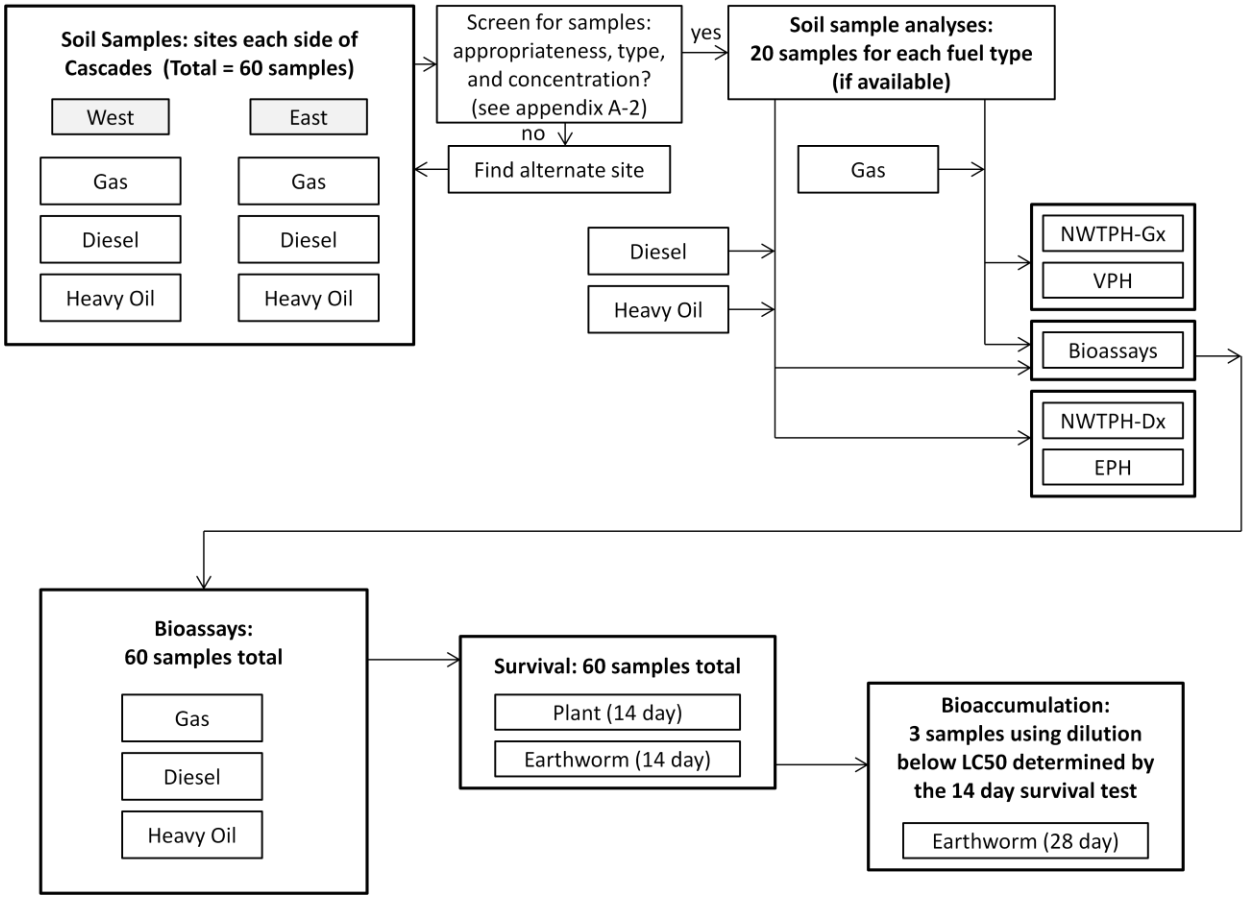

Figure A-1. Sample design.

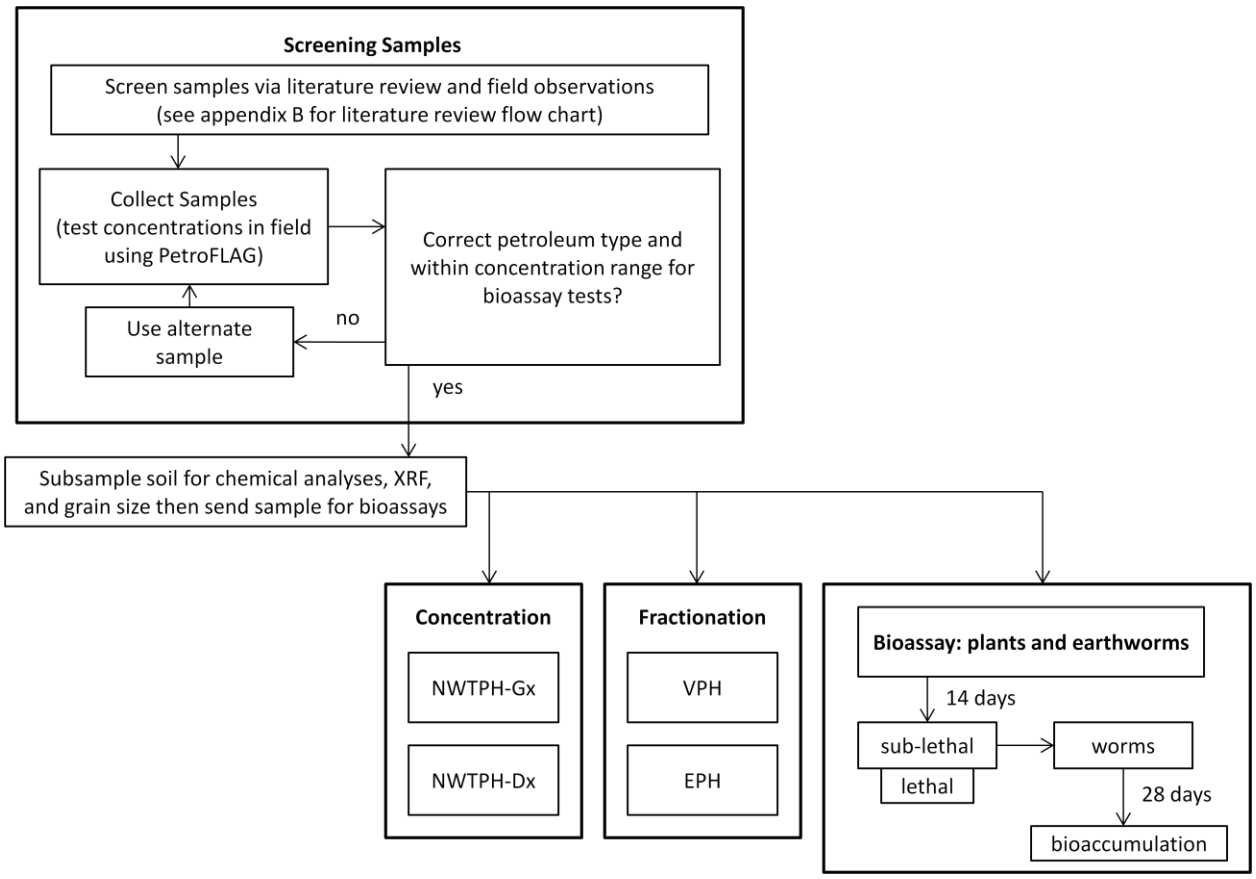

Figure A-2. Sample screening, collection, and analyses.

Appendix B. Site Selection: Literature Review Flow Chart

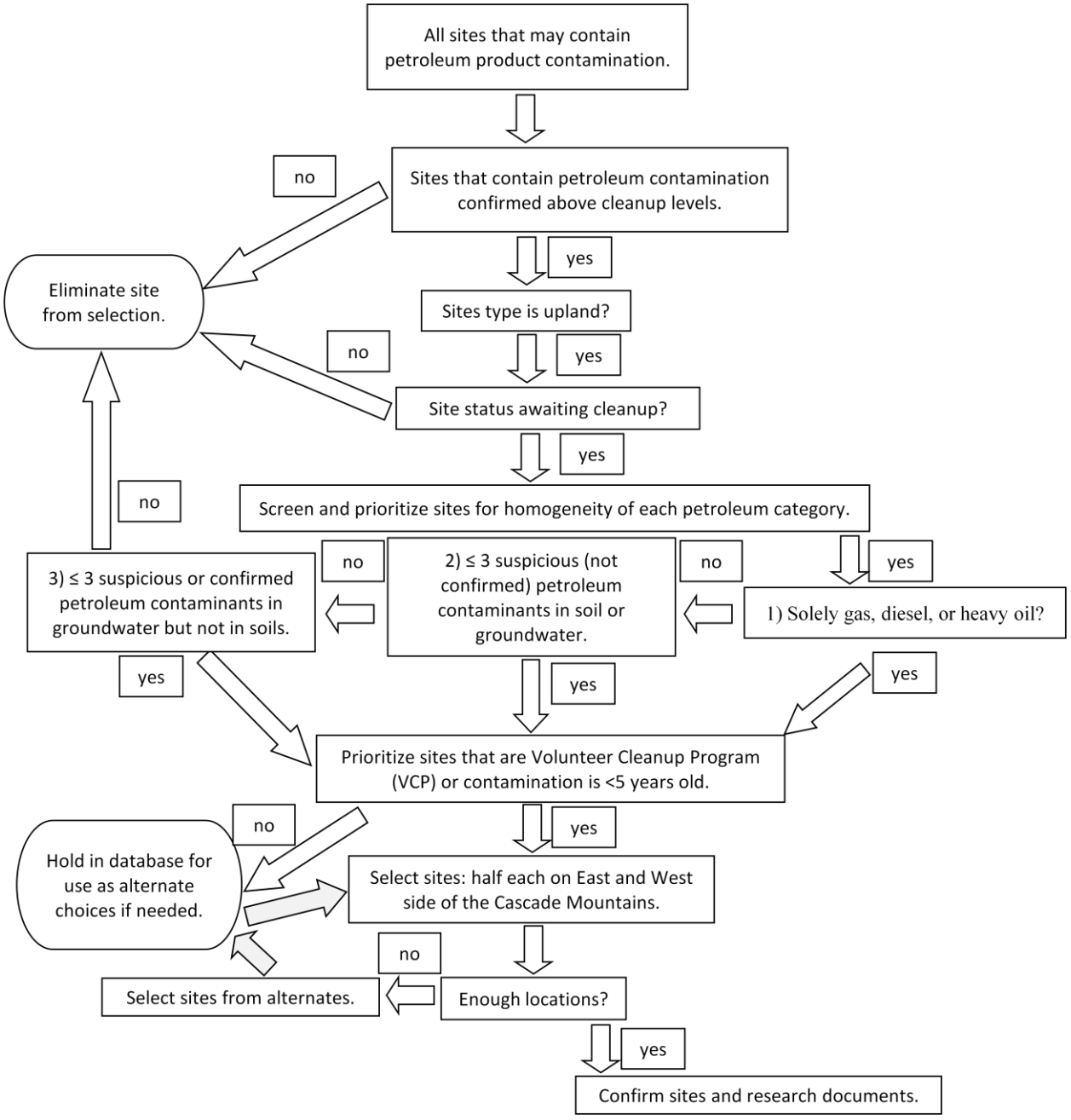

Figure B-1. Site selection literature review flow chart.

Appendix C. Soil Characteristics

Soil descriptions for this study are using portions of a modified version of ASTM standards D 2488 (ASTM, 2009; Ecology, 2011b). Identification will be based on visual-manual procedures. Soil descriptions include assessment of color, odor, moisture condition, soil structure, consistency, cementation, particle sizes, and other observations as noted at the time of sampling. Additional descriptions for identifying color, soil types, and plasticity are included below.

Color

The color should be described when the sample is first retrieved since the color will change with water content. Primary colors should be used (brown, gray, black, green, white, yellow, red). Describe soils with different shades or tints of basic colors by using two basic colors such as gray-green. Describe soil that is marked with spots of color as mottled. Soils with homogeneous texture but have color patterns can be described as streaked. The simplified color chart in Figure C-1 can be used as a reference.

Soil Type

Soil types are defined on the basis of texture with particle-size designators separating the soil into coarse-grained, sands, fine-grained, and highly organic designations. Use Table C-1 to define soil types.

Field Identification Tests for Plasticity

A Smear Test can be accomplished by taking a fragment of soil and smearing it between the thumb and forefinger or drawn across the thumbnail. A rough texture and dull smear indicates low plasticity, while a slick, waxy smear surface indicates soil of high plasticity.

Conduct a Thread Test by adding moisture or working moisture out of a small ball (about 1½ inch diameter) of soil. Add small amounts of moisture or soil until a ball can be formed. Knead the ball of soil until its consistency is medium stiff to stiff and it breaks or crumbles. A thread is then rolled out between the hands to the smallest diameter possible before it disintegrates. The smaller the thread achieved, the higher the plasticity of the soil. High plasticity will have threads smaller than 1/32 inch in diameter and will indicate fine-grained soils. Low plasticity will have threads larger than 1/8 inch in diameter. Table C-2 gives a guideline for plasticity.

Figure C-1. Basic soil colors taken from field descriptions of soils (Bartlett, 2012).

Table C-1. Soil classification (simplified from ASTM D 2488).

Major divisions	
Classification for sample < 3 inch (75 mm) sieve	**Coarse Grained Soils** Mass retained on or above No. 4 (4.75 mm) sieve.
	Sandy Soils Mass retained on or above No. 40 (0.420 mm) and No. 200 (0.075 mm) sieve.
	Fine Grained Soils Mass passed through No. 200 (0.075 mm) sieve.
	Highly Organic Soils Peat, muck, and other highly organic soils.

Table C-2. Plasticity field test descriptions (modified from Bartlett, 2012).

Plastic Range	Plasticity Description	Dry Strength	Smear Test	Thread Smallest Diameter inches (mm)	ML & MH (silt)	CL & CH (clay)	OL & OH (organic silt or clay)
0	non-plastic	None: crumbles into powder with mere pressure	gritty or rough	ball cracks	-	-	silt
1 – 10	low plastic	Low: crumbles into powder with finger pressure	rough to smooth	1/4 to 1/8 (3 to 6)	-	silty	silt
>10 – 20	medium plastic	Medium: breaks into pieces or crumbles with more finger pressure	smooth and dull	1/16 (0.5 to 1)	clayey	silty to clayey	clayey silt
>20 – 40	highly plastic	High: won't break with finger pressure but will break between thumb and a hard surface	shiny	1/32 (0.75)	clayey	-	silty clay
>40	very plastic	Very high: won't break between thumb and a hard surface	very shiny and waxy	1/64 (0.5)	clayey	-	organic

Appendix D. Glossary, Acronyms, and Abbreviations

Glossary

Bioaccumulation: General term describing a process by which chemicals are taken up by an organism either directly from exposure to a contaminated medium or by consumption of food containing the chemical.

Bioavailability: The presence of a substance in a form that organisms can take up.

NWTPH-Dx: The qualitative and quantitative method (extended) for semi-volatile ("diesel") petroleum products in soil and water.

NWTPH-Gx: The qualitative and quantitative method (extended) for volatile ("gasoline") petroleum products in soil and water.

NWTPH-HCID: A qualitative and semi-quantitative screen to determine the presence and type of petroleum products that may exist in water or soil.

Model Toxic Control Act (MTCA): A comprehensive regulatory scheme to identify, investigate, and clean up contaminated properties that are, or may be, a threat to human health or the environment.

Parameter: A physical chemical or biological property whose values determine environmental characteristics or behavior.

pH: A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

XRF: Instrument that measures metals concentrations using X-rays.

90th percentile: A statistical number obtained from a distribution of a data set, above which 10% of the data exists and below which 90% of the data exists.

Acronyms and Abbreviations

AL_EC	Aliphatic equivalent carbon number
AR_EC	Aromatic equivalent carbon number
BAF	Bioaccumulation Factor
CL	Contract lab
EC	Equivalent carbon number
e.g.	For example
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database

EPA	U.S. Environmental Protection Agency
EPH	Extractable Petroleum Hydrocarbons
et al.	And others
GIS	Geographic Information System software
GPS	Global Positioning System
i.e.	In other words
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
MTCA	Model Toxic Control Act
NWTPH-Dx	Northwest TPH hydrocarbon-Dx (extended)
NWTPH-Gx	Northwest TPH hydrocarbon-Gx (extended)
NWTPH-HCID	Northwest TPH hydrocarbon Identification
PCB	Polychlorinated biphenyls
PQL	Practical quantitation limit
QA	Quality assurance
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedures
TOC	Total organic carbon
TPH	Total petroleum hydrocarbon
VPH	Volatile Petroleum Hydrocarbons
WAC	Washington Administrative Code
WRIA	Water Resource Inventory Area
XRF	X-ray fluorescence instrument

Units of Measurement

°C	degrees centigrade
dw	dry weight
g	gram, a unit of mass
kg	kilograms, a unit of mass equal to 1,000 grams
mg	milligram
mL	milliliters
mm	millimeter
ppm	parts per million
ug/g	parts per million
ww	wet weight