DEPARTMENT OF
ECOLOGY
State of Washington

Quality Assurance Project Plan

Screening for PAHs and Metals in the Puget Sound Basin at Aquatic Habitats Adjacent to Mainline Railroad Tracks

October 2016

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This Quality Assurance Project Plan is available on Ecology's website at https://fortress.wa.gov/ecy/publications/SummaryPages/1603119.html

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October 2016

Approved by:

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Signatures are not available on the Internet version.
EAP: Environmental Assessment Program
HWTR-RTT: Hazardous Waste and Toxics Reduction Program-Reducing Toxic Threats
NRDA: Natural Resource Damage Assessment

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2.0 Abstract

Prior studies by Ecology and others have identified polycyclic aromatic hydrocarbons (PAHs) as an impact to water quality in Puget Sound. A Puget Sound Toxics Loading Analysis (PSTLA) study reported the presence of PAHs in a number of areas where concentrations potentially impacted aquatic life. As part of another statewide program Ecology's Reducing Toxic Threats Initiative, a Chemical Action Plan (CAP) was developed for PAHs, highlighting creosote-treated railroad ties as potentially the single largest initial release of PAHs to land and air in Washington State.

In response to recommendations in the PAH CAP, Ecology conducted a study to identify and map aquatic areas located along railroad tracks. The study recommended environmental monitoring be conducted to evaluate PAH levels in areas where surface waters are adjacent to railroad lines.

Recently rail shipments of coal and oil have increased through Washington. With these increases comes the greater potential for release to the environment. Heavy metals are also a concern for contamination from rail activities. To date, Ecology has not conducted studies establishing baseline levels of PAHs or metals contamination along railroads. Establishing baseline concentrations of PAHs and metals is important to track future changes in these contaminants from rail activities. Study results may also provide insight into PAH or metals migration from railroad lines to surface waters.

Ecology will conduct a baseline study to establish PAH and metals levels in soil, sediment, and water at 11 mainline railroad track sites. Study site locations were selected based on their access for sampling and include railroad lines through publically owned parks, and within the intertidal zone of marine waters, or beyond right-of-way boundaries for freshwater. Results will establish baseline PAH and metals concentrations at 11 sites for the area between mainline railroad tracks and surface waters.

3.0 Background

In recent years the Department of Ecology (Ecology) and others have identified polycyclic aromatic hydrocarbons (PAHs) as an impact to the water quality of Puget Sound in a number of studies (Norton et al., 2011; Davies et al., 2012; Sandvik, 2013). Between 2007 and 2011, Ecology and other groups conducted the Puget Sound Toxics Loading Analysis (PSTLA). The PSTLA reported PAHs were present in a number of areas of the Puget Sound basin at concentrations where effects are documented or at levels above criteria used to protect aquatic organisms and their consumers. PAH releases can be placed generally in two categories: combustion emissions are about 55% and releases from creosote-treated wood products are roughly 33% (Norton et al., 2011). Other potential sources of PAH to the environment are releases of coal, petroleum/fuel spills, and diesel emissions. The PSTLA is available at https://fortress.wa.gov/ecy/publications/publications/1103055.pdf

Another Ecology effort considered all of Washington State as part of the Reducing Toxic Threats Initiative and involved developing Chemical Action Plans (CAPs) for persistent, bioaccumulative, and toxic chemicals (PBTs). Considered the “worst of the worst”, PBTs remain in the environment for a long period of time and can be transported long distances moving between air, land, and water media. PAHs are a group of compounds that have been identified as a PBT and subsequently Ecology released a PAH CAP in 2012 describing uses and releases within Washington State (Davies et al., 2012). The PAH CAP is available at: https://fortress.wa.gov/ecy/publications/SummaryPages/1207048.html.

Recognizing the high percentage of the annual PAH release to land (81%) from railroad ties statewide the PAH CAP recommended a mapping exercise be conducted to evaluate where railroads intersect with sensitive aquatic areas (Davies et al. 2012). Sensitive aquatic areas near active railroads in Washington State were defined as areas with railroads near streams supporting salmonids, areas of Priority Habitat and Species (PHS), and wetlands included in the Northwest Wetland Inventory (NWI). Ecology conducted the mapping work in 2013 called, *Location of Creosote-Treated Railroad Lines near Sensitive Near-Shore Aquatic Habitats in Washington State*, (Sandvik, 2013). This evaluation combined mapping of aerial photography and GIS data layers to identify railroad track locations within 300 feet of “sensitive aquatic habitat”. The study recommended that the information be used to conduct environmental sampling to determine if PAHs are impacting “sensitive aquatic habitat”. The mapping exercise is available at: https://fortress.wa.gov/ecy/publications/documents/1303025.pdf

Coal and oil shipments by rail through Washington have been significantly increasing in recent years. Creosote is made up largely of PAHs, and creosote-treated wood railroad ties still represent the majority of ties used in railroad operations. Railroad operations have a number of possible sources of PAHs in addition to the creosote-treated railroad ties. PAHs are also significant components of fossil fuels so coal and oil are potential PAH sources to the environment. Metals also play a role in railroad activities, in addition to their being contaminants in coal and crude oil. This study will establish baseline levels of PAHs and metals along mainline railroad tracks in the Puget Sound basin.

3.1 PAHs, Alkyl-PAHs, TPH, and Metals

3.1.1 PAHs

PAHs are a group of around 10,000 compounds characterized by two or more aromatic (benzene) rings of carbon and hydrogen. In the environment PAHs are almost always found as a mixture. Of the numerous possible compounds, 16 have been the focus of the majority of research and are considered priority pollutants (pp) by the United States Environmental Protection Agency (USEPA) under the federal Clean Water Act (e-CFR, 2016). The International Agency for the Research on Cancer (IARC) suggests that several are known as possible or probable carcinogens for humans (IARC, 2010). The pp PAHs are usually divided into three groups: low molecular weight polycyclic aromatic hydrocarbons (LPAHs); high molecular weight polycyclic aromatic hydrocarbons (HPAHs); and carcinogenic polycyclic aromatic hydrocarbons (cPAHs). The 16 pp PAHs are listed below:

Low Molecular Weight PAHs (LPAHs)
- Acenaphthene
- Acenaphthylene
- Anthracene
- Fluorene
- Naphthalene
- Phenanthrene

High Molecular Weight PAHs (HPAHs)
- Benzo(a)anthracene*
- Benzo(a)pyrene*
- Benzo(b)fluoranthene*
- Benzo(k)fluoranthene*
- Benzo(g,h,i)perylene
- Chrysene*
- Dibenzo(a,h)anthracene*
- Fluoranthene
- Indeno(1,2,3-c,d)pyrene*
- Pyrene

*Designated as probable human carcinogens by EPA (cPAHs).

Generally speaking, the LPAHs are more water-soluble and volatile than the HPAHs. The HPAHs tend to be more resistant to oxidation, reduction, and vaporization and have less ability to dissolve in water. The LPAHs have significant acute toxicity to aquatic organisms, whereas the HPAHs do not. While the HPAHs do not exhibit toxicity to aquatic organisms like the LPAHs, of the 10 HPAHs seven of them make up the cPAH group, designated as probable human carcinogens.

3.1.2 Alkyl PAHs

Alkylated PAHs are more abundant, generally persist for a longer time, and are sometimes more toxic than the parent PAH. Alkyl substitution usually decreases water solubility, while also tending to bioaccumulate to a greater degree. Within a PAH family series toxicity increases with increasing alkyl substitution. Alkyl substituted PAHs may have phototoxicity potential compared to the parent or unsubstituted compounds (Irwin et al., 1997). These characteristics could be considered more of a toxic threat to the environment than their parent PAH compounds, even though they don’t have water quality criteria.

Selected alkyl PAHs will also be measured in addition to the EPA's 16 pp PAHs described above. Targeted alkyl PAHs are from the EPA's 16 pp PAHs, or parent PAH compounds, that have one or more alkyl group attachments. A number of petroleum related PAHs have alkyl group substitution on their ring structure. These alkyl groups generally have one to four saturated carbon atoms which can make many structural isomers and homologs possible for each PAH family. Crude oils contain primarily the alkyl homologs of aromatic compounds and relatively small quantities of the unsubstituted parent aromatic structures (Irwin et al., 1997). The target alkyl PAHs are listed below:

Alkyl PAHs

- 2-Chloronaphthalene
- 1-Methylnaphthalene
- 2-Methylnaphthalene
- 2,6-Dimethylnaphthalene
- 1,6,7-Trimethylnaphthalene
- 3,6-Dimethylphenanthrene
- 1-Methylphenanthrene
- 2-Methylphenanthrene
- Dibenzothiophene
- C1-Naphthalenes
- C2-Naphthalenes
- C3-Naphthalenes
- C4-Naphthalenes
- C1-Fluorenes
- C2-Fluorenes
- C3-Fluorenes
- C1-Dibenzothiophenes
- C2-Dibenzothiophenes
- C3-Dibenzothiophenes
- C1-Phenanthrenes/Anthracenes
- C2-Phenanthrenes/Anthracenes
- C3-Phenanthrenes/Anthracenes
- C4-Phenanthrenes/Anthracenes
- C1-Fluoranthene/Pyrene
- C1-Chrysenes
- C2-Chrysenes
- C3-Chrysenes
- C4-Chrysenes

The abundance, persistence, and potential toxicity of alkyl PAHs is a concern for the environment. While alkyl PAHs do not have water quality criteria their presence in combination with other toxic contaminants can provide information on the potential toxicity at a site while also establishing a baseline for future comparison.

3.1.3 TPH

In addition to the PAH and alkyl PAH analyses, the diesel fraction of total petroleum hydrocarbons (TPH-dx) will be measured in soil and sediments. This analysis is more specific to semi-volatile petroleum products and the diesel range of hydrocarbons. Although there isn't a total PAH criterion available in the Sediment Management Standards (SMS), there is a freshwater criterion available for TPH.

3.1.4 Metals

As defined in the 1977 Clean Water Act priority pollutants are a subset of “toxic pollutants”. The EPA used four criteria to select priority pollutants:

- Pollutant is specifically named on the list of toxic pollutants.
- A chemical standard is available for the pollutant, enabling analysis of the pollutant.
- The pollutant had to be reported as found in water with a frequency of occurrence of at least 2.5%.
- The pollutant was produced in significant quantities, as reported in Stanford Research Institute’s “1976 Directory of Chemical Producers, USA.”

The EPA has a published list of approved analytical methods for priority pollutant analyses. Priority pollutants are listed because they can cause death, illness, mutations, behavioral abnormalities, or physiological malfunctions in living organisms. Priority pollutant metals include 13 selected metals as a subset of the priority pollutants. Five are known human carcinogens, while four others are suspected carcinogens. Soil and sediment samples will be analyzed as “total recoverable metals“, while water samples will be analyzed as “dissolved metals”. The target pp metals are listed below:

pp Metals

Antimony (Sb)[2]
Arsenic (As)[1]
Beryllium (Be)[1]
Cadmium (Cd)[1]
Chromium (Cr)[1]
Copper (Cu)
Lead (Pb)[2]
Mercury (Hg)[2]
Nickel (Ni)[1]
Selenium (Se)
Silver (Ag)
Thallium (Tl)[2]
Zinc (Zn)

[1] Known human carcinogen
[2] Suspected human carcinogen

3.1.5 PAHs and metals sources

Many potential PAH and metals sources along rail corridors are associated with trains and their tracks. Creosote has been reported to contain over 30 PAHs and a total PAH content of up to 85% by weight (WHO, 2004). Other sources of PAHs can vary. Some are created naturally; others are man-made. During low temperature burning of materials such as coal, gas, oil, or garbage (organics), PAHs are created and released. Releases to the air are thought to be mostly from volcanoes, forests fires, residential wood burning, and exhaust from cars and trucks. Direct sources to surface water are through industrial discharges, waste treatment plants, and stormwater. PAHs can also be released to soils at hazardous waste sites escaped from storage (ATSDR, 1995). Along rail corridors, metals are a product of friction between the wheel and rails, wheel and brake pads. Metals are also contained in some fluids and greases (Wilkomirski, 2012). Metal impurities are also known to be associated with coal and crude oil.

Total annual releases of PAHs to the Puget Sound basin are estimated at 310,000 kg/year. In general, PAH releases can be placed in two categories: combustion emissions and releases from creosote-treated wood products. Combustion releases account for about 55% while creosote-treated wood products are about one-third of the PAH release (Norton et al., 2011). Releases of coal, petroleum/fuel spills, and diesel emissions are other potential sources of PAHs to the environment.

The PSTLA reported estimates of annual loading for selected metals through major pathways to the Puget Sound (Norton et al., 2011). Median range estimates of total mercury and total cadmium loads were 0.21 and 0.28 metric tons, respectively. Median annual loads reported for total lead, total arsenic, total copper, and total zinc were 7.0, 18, 45, and 170 metric tons per year, respectively.

3.2 Study area and surroundings

The National Estuary Program (NEP) is funding the study. Western Washington and the Puget Sound region's drainages, wetlands, or waterways are targeted for site selection due to the source of funding. This study will use publicly owned lands in the Puget Sound basin to access study sites where surface water is located within 50 feet of the railroad right-of-way. Locations of study sites are shown on Figure 1.

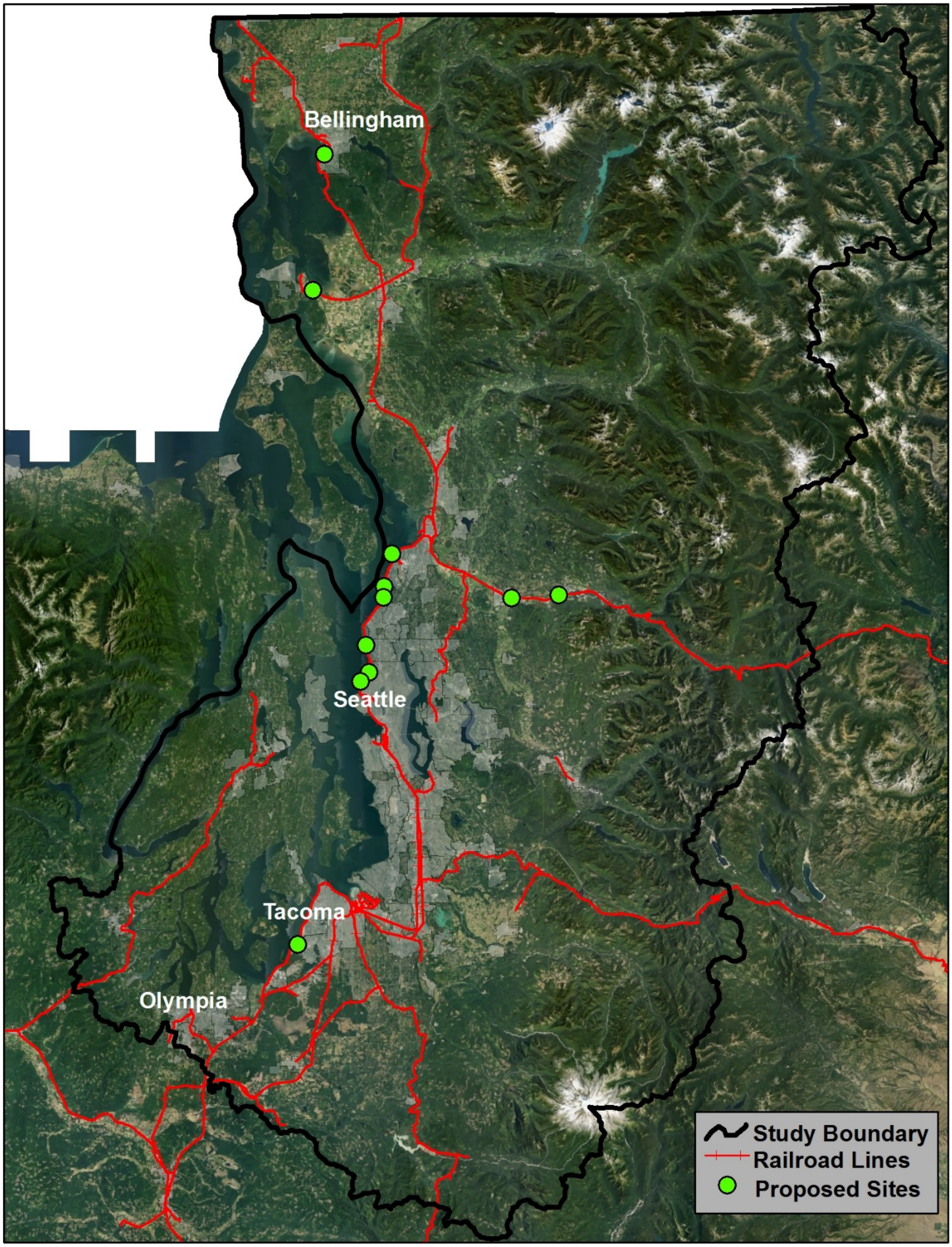

Figure 1. Study area and sample sites.

3.2.1 Logistical problems

Selection of sampling sites was limited by not having access to the railroad right-of-way. Railroad lines and their right-of-ways are privately owned by the railroads and would require permission to access. The railroads would not grant permission to Ecology for accessing their property. As an alternative sample sites will be accessed through publicly owned land. Railroad lines or their right-of-ways will not be accessed for sample collection. All sample locations were selected following a site reconnaissance and were based on the ability to sample between the railroad right-of-way and surface water without trespassing on railroad property.

3.2.2 History of study area

Created by glaciers, the Puget Sound is a northwest fjord. The source of marine waters to the Puget Sound is the Pacific Ocean by way of the Strait of Juan de Fuca. Additionally, the Sound receives large freshwater inflows such as the Cedar, Duwamish/Green, Elwha, Nisqually, Nooksack, Puyallup, Skagit, Skokomish, Snohomish, and Stillaguamish Rivers.

As the first European settlement in the Puget Sound, the Hudson’s Bay Company built a fur trading post in 1833 called Fort Nisqually. In 1845 Tumwater, originally known as New Market, was established as the first American settlement on Puget Sound founded by Americans crossing the continent by way of the Oregon Trail. The Northern Pacific Railroad reached the Puget Sound in 1888, linking the Northwest to eastern states. The next year Washington became a state on November 11, 1889 (Quinn, 2010).

Around the mid-1800s logging started in the Puget Sound. Seattle was known for being the area’s largest port for trade and shipbuilding and Tacoma was known for smelting of gold, silver, copper, and lead ores. Along with the establishment of the railroad, the majority of regional industry and development was located on the eastern Puget Sound.

3.2.3 Parameters of interest

The parameters to be sampled for the study are pp PAHs (16), alkylated PAHs, TPH, and pp metals (13). Seven of the 16 pp PAHs are considered by the International Agency for the Research on Cancer (IARC, 2010) as possible or probable carcinogens for humans. Five of the 13 pp metals are known human carcinogens, while four others are suspected carcinogens. For sediment and soil samples, companion total organic carbon (TOC) and grain size will also be analyzed. TOC in sediment can moderate toxic effects of PAHs (NYSDEC, 2014). In addition some numeric sediment criteria require TOC normalized PAH concentrations for comparison. For water samples in addition to PAHs and metals, dissolved organic carbon (DOC) and hardness will be analyzed. The ancillary parameters TOC, DOC, hardness, and grain size may be used to normalize results for site-to-site comparisons (see section 7.1.3).

3.2.4 Results of previous studies

Ecology has not conducted prior studies for PAHs or metals along railroad lines.

3.2.5 Regulatory criteria or standards

The Washington State sediment cleanup levels contained in WAC 173-204-563, apply to freshwater sediments based on protection of the benthic community from toxicity. These Sediment Management Standards (SMS) chemical criteria have not established acute or chronic adverse effect objectives but assume values below the sediment cleanup concentration corresponds to sediment quality resulting in no adverse effects to the benthic community. Sediment criteria are detailed in Table 1.

Water quality criteria for PAHs do not have a threshold for total PAH. Eleven of the 16 pp PAHs in water criteria are from the National Toxics Rule (NTR) for human health and are listed below in Table 1. Currently alkylated PAHs are not included in water quality criteria.

Table 1. Washington State Sediment and Water Quality Criteria for PAHs and metals.

Analyte	Matrix	Regulatory Criteria	Carcinogen/ Non-carcinogen	Criterion Concentration
Sediment - Freshwater				
Total PAHs	Sediment	SMS[1]	NA	17,000 ug/Kg, dw
TPH (Diesel)	Sediment	SMS	NA	340 mg/Kg, dw
Arsenic	Sediment	SMS	NA	14 mg/Kg, dw
Cadmium	Sediment	SMS	NA	2.1 mg/Kg, dw
Chromium	Sediment	SMS	NA	72 mg/Kg, dw
Copper	Sediment	SMS	NA	400 mg/Kg, dw
Lead	Sediment	SMS	NA	360 mg/Kg, dw
Mercury	Sediment	SMS	NA	0.66 mg/Kg, dw
Nickel	Sediment	SMS	NA	26 mg/Kg, dw
Selenium	Sediment	SMS	NA	11 mg/Kg, dw
Silver	Sediment	SMS	NA	0.57 mg/Kg, dw
Zinc	Sediment	SMS	NA	3200 mg/Kg, dw
Soil				
TPH (Diesel)	Soil	MTCA[2]	NA	2,000 mg/Kg[3]
Benzo(a)pyrene	Soil	MTCA	C	0.1 mg/Kg
Arsenic	Soil	MTCA	C	20 mg/Kg
Cadmium	Soil	MTCA	C	2 mg/Kg
Chromium (VI)	Soil	MTCA	C	19 mg/Kg
Lead	Soil	MTCA	S	250 mg/Kg
Mercury	Soil	MTCA	S	2 mg/Kg
Freshwater				
Anthracene[5]	Water	NTR[4]	NC	9,600 ug/L
Fluorene[5]	Water	NTR	NC	1,300 ug/L

Analyte	Matrix	Regulatory Criteria	Carcinogen/ Non-carcinogen	Criterion Concentration
Benzo(a)anthracene[6]	Water	NTR	C	0.0028 ug/L
Benzo(a)pyrene[6]	Water	NTR	C	0.0028 ug/L
Benzo(b)fluoranthene[6]	Water	NTR	C	0.0028 ug/L
Benzo(k)fluoranthene[6]	Water	NTR	C	0.0028 ug/L
Chrysene[6]	Water	NTR	C	0.0028 ug/L
Dibenzo(a,h)anthracene[6]	Water	NTR	C	0.0028 ug/L
Fluoranthene[6]	Water	NTR	NC	300 ug/L
Indeno (1,2,3-c,d)pyrene[6]	Water	NTR	C	0.0028 ug/L
Pyrene[6]	Water	NTR	NC	960 ug/L
Antimony	Water	NTR	NC	14 ug/L
Arsenic	Water	NTR	C	0.018 ug/L
Mercury	Water	NTR	S	0.14 ug/L
Nickel	Water	NTR	NC	610 ug/L
Thallium	Water	NTR	NC	1.7 ug/L
Arsenic	Water	WAC[7]	C	190.0 ug/L
Cadmium	Water	WAC	C	$<(CF)(e^{(0.7852[\ln(\text{hardness})]-0.3490)})$[8]
Chromium	Water	WAC	C	10.0 ug/L[9]
Copper	Water	WAC	NC	$<(0.960)(e^{(0.8545[\ln(\text{hardness})]-1.465)})$
Lead	Water	WAC	S	$<(CF)(e^{1.273[\ln(\text{hardness})]-4.705)})$[10]
Mercury	Water	WAC	S	0.012 ug/L[11]
Nickel	Water	WAC	NC	$<(0.997)(e^{(0.8460[\ln(\text{hardness})]+1.1645)})$
Selenium	Water	WAC	NC	5.0 ug/L[11]
Silver	Water	WAC	NC	$<(0.85)(e^{(1.72[\ln(\text{hardness})]-6.52)})$[12]
Zinc	Water	WAC	NC	$<(0.986)(e^{(0.8473[\ln(\text{hardness})]+0.7614)})$

[1] Sediment Management Standards (SMS), sediment cleanup objectives (SCO).
[2] Model Toxics Control Act (MTCA), Method "A" soil cleanup levels
[3] TPH criterion is the MTCA diesel range organics criterion.
[4] National Toxics Rule (NTR) for human health, Freshwater-water and organisms.
[5] LPAHs.
[6] HPAHs.
[7] Washington Administrative Code – WAC 173-201A, for the protection of aquatic life, chronic.
Values are the chronic criterion unless otherwise noted.
[8] CF is the conversion factor for cadmium. CF=1.101672 – [(ln hardness)(0.041838)].
[9] Conversion factor for total chromium to dissolved chromium is 0.962.
[10] CF is the conversion factor for lead. CF=1.46203 – [(ln hardness)(0.145712)].
[11] Based on Total Recoverable.
[12] Acute criterion only, no chronic value.
NA: Not applicable.
NC: Non-carcinogenic.
C: Carcinogenic.
S: Suspected human carcinogen.

4.0 Project Description

The proposed study will generate baseline PAHs and metals concentrations within the Puget Sound basin downgradient of mainline railroad tracks. Ecology's Environmental Assessment Program (EAP) will conduct the study. Soil, sediment, and water samples will be collected within western Washington's Puget Sound drainage at 11 sites. Sample locations were selected that were located on publically owned land within 50 feet of a mainline railroad right-of-way to surface water draining into the Puget Sound basin.

Sampling from publically owned land will allow samples to be collected near railroad tracks without violating railroad property rights. Marine sites will be accessed within the intertidal zone of marine waters. These areas are sheltered areas directly adjacent to the rail lines. Sites will be sampled just beyond the railroad right-of-way boundary. Selection of sites for the project was limited to areas within the Puget Sound basin because NEP is funding this project.

Sediment and soil samples will be analyzed for the pp PAHs (16), alkylated PAHs, TPH, and total recoverable metals (13), along with TOC and grain size. Fresh water samples will be collected and also analyzed for the 16 pp PAHs, alkylated PAHs, dissolved metals (13), hardness, and dissolved organic carbon (DOC). Manchester Environmental Laboratory (MEL) will conduct the chemical analyses of sediment, soil, and water. The grain size analysis will be contracted out. A baseline for PAHs and metals concentrations will be established while applicable sediment or water quality standards will be compared to study results.

4.1 Project goals

The goal of the study is to determine current levels of pp PAHs and metals within railroad corridors near aquatic habitats in the Puget Sound basin.

4.2 Project objectives

Specific objectives of the study are to:

- Collect soil, sediment, and freshwater water samples downgradient of mainline railroad tracks adjacent to surface waters around the Puget Sound on publically owned land. Analyze samples for PAHs, metals, TPH, TOC, DOC, hardness, and grain size.
- Establish baseline PAH and metals levels in soils and sediment downgradient of mainline railroad tracks for future comparisons.

4.3 Information needed and sources

Specific knowledge of PAHs and metals levels in sediment, soil, and water from within Puget Sound basin railroad corridors is not currently available. Studies have not been completed in Washington to establish these baseline conditions so the information is not currently available. Data generated from this study may be compared to other study data found in Ecology's Environmental Information Management database (EIM) system reporting recent PAHs and metals results from soils, sediments, or freshwater.

4.4 Target population

The target population is PAHs and metals from railroad lines to soils, sediment, and surface waters of the Puget Sound basin.

4.5 Study boundaries

Because the funding source is the National Estuary Program (NEP), the study area is western Washington and the Puget Sound drainages, wetlands, or waterways. See Figure 1.

Water Resource Inventory Areas (WRIA) numbers for the study area:

WRIAs 5 through 17 are all candidate watersheds for site selection.

4.6 Tasks required

Planned activities for the project's study are listed below.

- Following review, receipt, and incorporation of comments from client reviewers for the Quality Assurance Project Plan (QAPP), the study will be conducted as planned.
- Samples will be collected once at eleven study sites: eight marine, and three freshwater.
- Study results will be evaluated and a report describing significant findings will be written.
- The study report will be reviewed by client reviewers and comments will be considered before the final document is published to the web.

4.7 Practical constraints

See Section 3.1.1.

4.8 Systematic planning process

This QAPP represents the systematic planning process for this project.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 2. Organization of project staff and responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Blake Nelson HWTR-RTT Program Headquarters Phone: 360-407-6940	EAP Client/Acting Unit Manager	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.
Alison Meyers NRDA Lead, Spills Program Phone: 360-407-7114	EAP Client	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.
Randy Coots Toxics Studies Unit SCS Phone: 360-407-6690	Project Manager/ Principal Investigator	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.
Siana Wong Toxics Studies Unit SCS Phone: 360-407-6432	Field Assistant	Helps collect samples and records field information.
Debby Sargeant Toxics Studies Unit SCS Phone: 360-407-6775	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Jessica Archer SCS Phone: 360-407-6543	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Dale Norton WOS Phone: 360-407-6596	Section Manager for the Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Joel Bird Manchester Environmental Laboratory Phone: 360-871-8801	Director	Reviews and approves the final QAPP.
Contract Laboratory	Project Manager	Reviews draft QAPP, coordinates with MEL QA Coordinator
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
HWTR-RTT: Hazardous Waste and Toxics Reduction-Reducing Toxic Threats
SCS: Statewide Coordination Section

5.2 Special training and certifications

The field team will be familiar with the following Ecology Standard Operating Procedures (SOPs):

EAP013 – Determining Coordinates via Hand-held Global Positioning System (GPS) Receivers (Janisch, 2006).
http://www.ecy.wa.gov/programs/eap/qa/docs/ECY_EAP_SOP_AssigningGPSCoordinates_v1_0EAP013.pdf

EAP015 – Manually Obtaining Surface Water Samples (Joy, 2006).
http://www.ecy.wa.gov/programs/eap/qa/docs/ECY_EAP_SOP_ManuallyObtainingSurfaceWaterSamples_v1_2EAP015.pdf

EAP040 – Freshwater Sediment Sampling (Blakley, 2008).
http://www.ecy.wa.gov/programs/eap/qa/docs/ECY_EAP_SOP_FreshWaterSedimentSampling_v1_1EAP040.pdf

EAP070 – Minimizing the Spread of Aquatic Invasive Species (Parsons et al., 2012).
http://www.ecy.wa.gov/programs/eap/qa/docs/ECY_EAP_SOP_MinimizeSpreadOfAIS_v2_0EAP070.pdf

EAP090 – Decontaminating Field Equipment for Sampling Toxics in the Environment (Friese, 2014).
http://www.ecy.wa.gov/programs/eap/qa/docs/ECY_EAP_SOP_EquipmentDeconToxicsSampling_v1_0EAP090.pdf

All field staff will be current on EAP safety and first aid training.

5.3 Organization chart

See Table 2.

5.4 Project schedule

Table 3. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	Due date	Lead staff
Field work starts	September 2016	Randy Coots
Field work completed	October 2016	Randy Coots
Laboratory analyses completed	January 2017	
Environmental Information System database (EIM)		
EIM Study ID	RCOO0016	
Product	Due date	Lead staff
EIM data loaded	February 2017	Siana Wong
EIM data entry review	March 2017	Melissa McCall
EIM complete	April 2017	Siana Wong
Final report		
Author lead / Support staff	Randy Coots	
Schedule		
Draft due to supervisor	April 2017	
Draft due to client/peer reviewer	May 2017	
Draft due to external reviewer(s)	June 2017	
Final (all reviews done) due to publications coordinator	July 2017	
Final report due on web	August 2017	

5.5 Limitations on schedule

Sample site locations were selected based on discussions with the Ecology Spills Program to prioritize sites for a baseline assessment for PAHs and metals. Sites require access and an ability to transport staff and sample collection equipment safely. The study will be conducted off railroad property or right-of-way. Permission was not granted to access railroad property. A site reconnaissance was required for proposed sample locations to determine acceptability.

5.6 Budget and funding

The estimated laboratory costs for this project total $88,281. Table 4 presents breakdown for these estimates. The NEP is funding the study. Western Washington and the Puget Sound region’s drainages, wetlands, or waterways were targeted for study site selection.

Table 4. Project budget and funding.

Parameter/Site	Matrix	Number of Sites	Samples per Site	Total Per Site + QA[1]	Cost Per Sample	MEL Subtotal	Contract Fee[2]
PAHs Marine	Soil	8	5	45	471	21,195	
TPH Marine	Soil	8	5	45	157	7065	
Metals Marine	Soil	8	5	45	206	9270	
PAHs Freshwater	Soil	3	5	18	471	8478	
TPH Freshwater	Soil	3	5	18	157	2826	
Metals Freshwater	Soil	3	5	18	206	3708	
PAHs Freshwater	Sediment	3	5	18	471	8478	
TPH Freshwater	Sediment	3	5	18	157	2826	
Metals Freshwater	Sediment	3	5	18	206	3708	
PAHs Freshwater	Water	3	3	11	417	4587	
Metals Freshwater	Water	3	3	11	195	2145	
Hardness Freshwater	Water	3	1	5	24	120	
DOC Freshwater	Water	3	1	5	39	195	
TOC	Soil or Sediment	11	70[3]	80	46	3680	
Grain Size	Soil or Sediment	11	70[3]	80	100	8,000	2000
				Laboratory Total		$88,281	

[1] Total reflects samples per site plus QA/QC.
[2] Contract fee includes a 25% additional charge.
[3] Survey total minus QA samples.

6.0 Quality Objectives

6.1 Decision Quality Objectives (DQOs)

NA

6.2 Measurement Quality Objectives

In addition to the MQOs shown below in Table 5, the quality of study results will be assured by collection and analysis of field replicates and blanks. Field replicates will be collected and analyzed at a minimum rate of 10 percent of the total for each study parameter. For the metals analyses, filter blanks will be analyzed for each day of sampling.

Table 5. Measurement Quality Objectives (MQOs).

Analyte	Lab Control Standards (% Recovery)	Laboratory Duplicates (RPD)[1]	Matrix Spike (% Recovery)	Matrix Spike Dupes (RPD)	Surrogate Recoveries (% Recovery)	Lowest Concentration of Interest
Soil or Sediment						
pp PAHs	40 – 150	≤50%	40 – 150	≤40%	10 – 150	1 ug/Kg
pp Metals	75 – 125	≤25%	70 – 130	≤25%	NA	0.1 mg/Kg[2]
TPH-Diesel	40 - 150	≤50%	NA	NA	NA	50 mg/Kg
TOC	75 – 125	≤20%	NA	NA	NA	0.1 ug/Kg
Grain Size	NA	≤20%[3]	NA	NA	NA	NA
Water						
pp PAHs	40 – 150	≤50%	40 – 150	≤40%	10 – 150	0.01 ug/L
pp Metals	75 – 125	≤25%	70 – 130	≤30%	NA	0.005 mg/L
Hardness	80 – 120	≤20%	75 – 125	≤25%	NA	1 mg/L
DOC	75 - 125	≤20%	NA	NA	NA	0.1 ug/L

[1] Relative percent difference.

[2] Fe=2.5 mg/Kg; Cr=0.5 mg/Kg; As, Be, and Cu=0.1 mg/Kg; Sb and Cd=0.05 mg/Kg; and Hg=0.005 mg/Kg.

[3] Laboratory triplicates are used for grain size analyses. Relative standard deviation (RSD) is used instead of relative percent difference (RPD).

6.2.1 Targets for precision, bias, and sensitivity

6.2.1.1 Precision

Precision is a measure of the variability in the results of replicate measurements due to random error. Precision is usually assessed by analyzing duplicate samples (or field measurements).

Laboratory duplicates consist of one sample thoroughly mixed and split into two separate samples in the laboratory, treated and analyzed exactly the same. Results reflect the amount of variability from the laboratory expected for the analysis. Variability should be low for duplicate pairs. Overall variability will be estimated based on analysis of field replicates. Field replicates consist of one sample collected immediately after the first and as close to the same time and place as possible. Field replicates would be expected to show a slightly higher variability than laboratory duplicates. See Table 5 above for acceptance criteria of duplicate precision.

6.2.1.2 Bias

Bias is the difference between the population mean and the true value. Bias will be addressed by analyzing lab control samples, matrix spikes, and surrogates. Targets for bias will be expressed in terms of acceptable % recovery (of a known quantity). See Table 5 for limits of acceptability for study analytes.

6.2.1.3 Sensitivity

Water quality results may be compared to available criteria. The analytical methods for PAHs and metals will need a level of sensitivity low enough to determine compliance with regulatory criteria. This may be more difficult for metals in water analyses comparing to the NTR without use of high resolution methods. The analytical method detection limits (MDLs) for PAHs and metals will attempt to be at or lower than water quality criteria. Section 3.2.5 *Regulatory criteria or standards* Table 1 lists the individual study parameters that have state or federal criteria. Sediment criteria in Table 1 is listed for total PAHs, total LPAHs, total HPAHs, and total recoverable metals, while water criteria is presented for 11 individual PAHs.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

No prior studies have been conducted by Ecology for PAHs and metals along railroad lines. Comparability of study results will be ensured by using standard operating procedures and adhering to established data quality criteria consistent with other studies analyzing PAHs and metals. Selection of analytical methods was based on the ability of the method to detect target analytes low enough to compare to the water quality standards and the overall needs of the study including the laboratory budget.

6.2.2.2 Representativeness

The sampling design was developed to obtain PAH and metals data representative of soil, sediment, and water from areas between surface waters or “aquatic habitats” and mainline railroad lines in the Puget Sound basin. Representativeness will be ensured by using appropriate sampling and sample handling procedures.

Ecology proposes to collect soil, sediment, and water samples from 11 sites in the Puget Sound basin. Sediment will be collected as three separate grabs, composited and homogenized for sub-sampling. Composite samples will reduce variability and better reflect average PAH and total recoverable metals concentrations. The fresh water sites targeted for the study are a small wetland and two major rivers. Fine-grained materials (silts and clay) will be targeted for sediment samples at the freshwater sites that are less than 50 feet from the railroad right-of-way. Soil and sediment samples will be collected from the top 2 cm horizon. Water samples will be collected from fresh water bodies in replicate as wrist depth grab samples. Table 4 above shows the proposed type and total number of study samples.

7.0 Sampling Procedures

7.1.1 Field measurements

At the three freshwater sample stations the conventional parameters temperature, pH, and specific conductance will also be measured by thermometer or probe within the water body.

7.1.2 Sampling location and frequency

Sample site locations have been selected and are shown on Figure 1. Sites will be sampled on one occasion. Table 6 below lists the sample locations, the adjacent water body, property ownership, and the latitude and longitude of each site. All sample locations except the March Point site are accessed through city, county, or state parks. The March Point site is along a county road and mainline railroad. The sampling location can be accessed from the county right-of-way or beyond the railroad right-of-way.

Table 6. Proposed study sites and locations.

Location	Adjacent Water body	Property Ownership	Latitude[1]	Longitude[1]
Sultan River Park	Sultan River and Skykomish River	City of Sultan	47.8606	-121.8202
Al Borlin Park	Woods Creek and Skykomish River	City of Monroe	47.8562	-121.9583
March Point	Small wetland	Washington State	48.4659	-122.5369
Lighthouse Park	Puget Sound	City of Mukilteo	47.9443	-122.3079
Picnic Point Park	Puget Sound	Snohomish County	47.8817	-122.3325
Meadowdale Beach Park	Puget Sound	Snohomish County	47.8609	-122.3349
Boulevard Park	Bellingham Bay	City of Bellingham	48.7334	-122.4998
Richmond Beach Park	Puget Sound	King County	47.7659	-122.3869
Carkeek Park	Puget Sound	City of Seattle	47.7131	-122.3790
Golden Gardens Park	Puget Sound	City of Seattle	47.6950	-122.4040
Steilacoom Park	Puget Sound	City of Steilacoom	47.1771	-122.5905

[1] NAD 83 HARN

7.1.3 Parameters to be determined

- Soil and sediment
    - PAHs, alkylated PAHs
    - metals, total recoverable
    - TOC
    - TPH – diesel fraction
    - grain size

- Water
  - PAHs
  - metals, dissolved
  - DOC
  - hardness

See Table 8 for expected range of results, reporting limits, and the clean-up and analytical methods proposed for the study.

7.2 Maps or diagram

Proposed sample locations are identified as green dots on a Puget Sound map shown in Figure 1. Below, Figure 2 presents an example sampling scheme for soils, sediment, and water samples to be collected for the study.

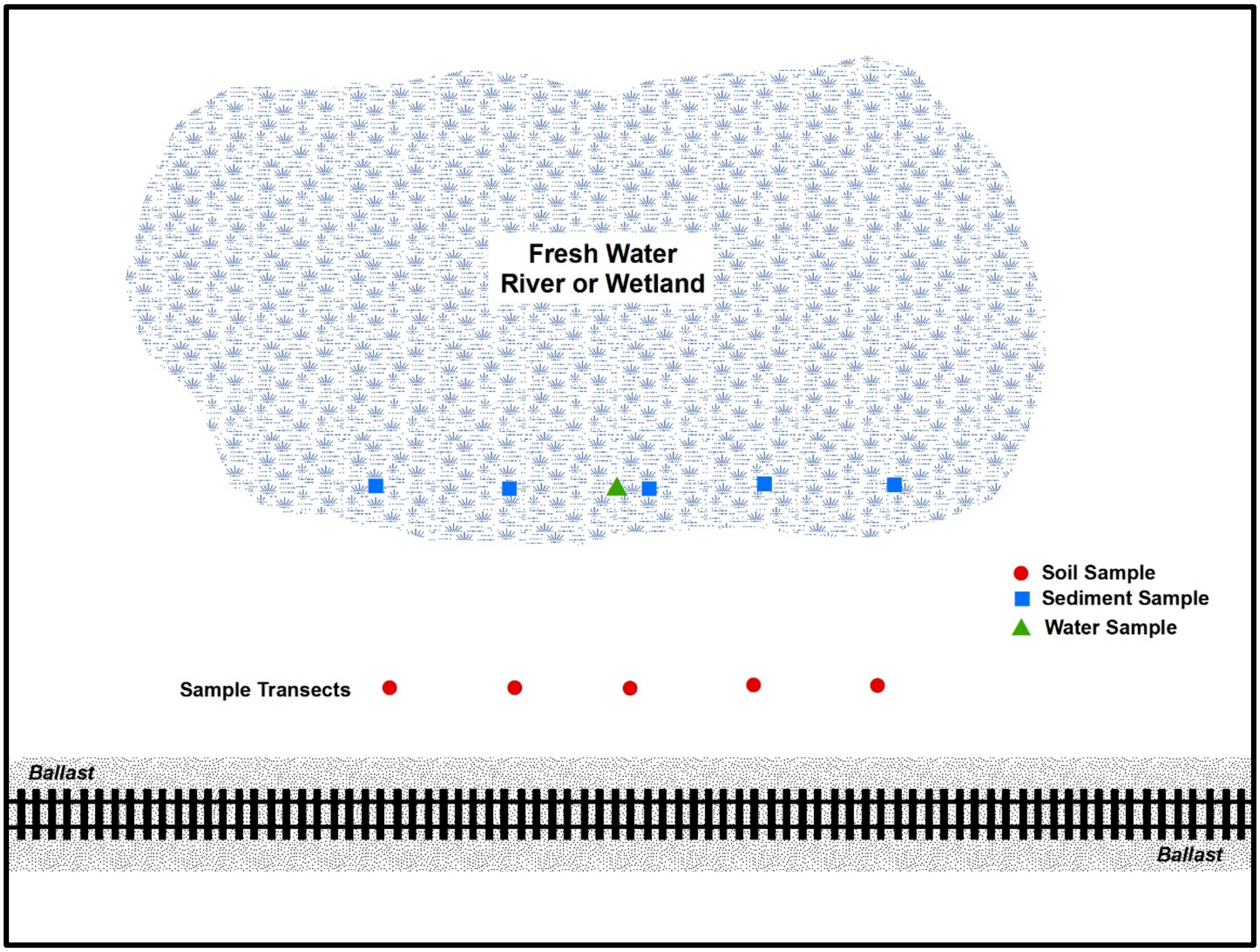

Figure 2. Transect sample scheme for soil, sediment, and water.

7.3 Assumptions underlying design

Suitable fine soil and sediment of an organic nature are assumed available at sample site locations. During site reconnaissance, we verified that soils and sediment were providing a significant amount of fine-grained material (particle size <62.5 *u*m).

Direct comparison from site to site or sample to sample may require result normalization. The ancillary parameters TOC, DOC, hardness, and grain size will be collected along with PAH and metals samples to ensure appropriate comparisons can be made.

7.4 Relation to objectives and site characteristics

The inability to get access to railroad right-of-ways has limited the study design to sites where access is through publically accessible lands.

7.5 Characteristics of existing data

NA

8.0 Measurement Methods

8.1 Field measurement and field sampling SOPs

Field SOPs are listed in section 5.2 Special training and certifications.

8.2 Containers, preservation methods, holding times

Sample containers, preservation, and holding time requirements for the study are shown in Table 7. Pre-cleaned sample containers will be obtained from the MEL prior to each sampling event. Containers will be suitable for the specific analyses to be performed. Containers will be free of contaminants according to USEPA (1992) and will meet quality assurance certification from the supplier.

Table 7. Study parameters, sample and container size, preservation, and holding times for soil, sediment, or water samples.

Parameter	Matrix	Minimum Quantity Required[1]	Container and Volume	Preservative	Holding Time
Soil or Sediment					
PAHs (16)	Soil or Sed	250 grams	8 oz glass	Cool to 4 °C; may freeze at -18°C	14 Days; 1 year frozen.
Metals (13)[2]	Soil or Sed	50 grams	4 oz glass	Cool to ≤6 °C	6 months
TPH-Diesel	Soil or Sed	250 grams	8 oz glass	Cool to ≤6 °C	14 days; 1 year frozen
TOC	Soil or Sed	25 grams	Certified 2 oz Glass w/ Teflon Lid Liner	Cool to 4 °C; may freeze at -18 °C	14 days; 6 months frozen
Grain Size	Soil or Sed	150 grams	8 oz Glass or Poly	Cool to 4 °C	6 months
Water					
PAHs (16)	Water	1000 mL	1 L Amber Glass	Cool to 4 °C	7 Days
Metals (13)	Water	1000 mL	1.0 liter Teflon	Field filtered 0.45 um, (#450-0045, type S)	Filter w/in 15 mins of collection, adjust pH to <2.0 w/HNO_3, cool to ≤6 °C
Hardness	Water	100 mL	125 mL poly	H_2SO_4 to pH ≤2, cool to ≤6 °C	6 months
DOC	Water	50 mL	60 mL Poly	Field Filter w/ 0.45 um; 1:1 HCl to pH<2; Cool to 4 °C	28 Days

[1] Laboratory minimum requested amount.

[2] Metals for soil and sediment analyzed as "total recoverable metals", while water samples analyzed as "dissolved metals".

8.3 Invasive species evaluation

An assessment of the potential for an invasive species contamination of gear and equipment was made after sample sites for the study were selected. No proposed sample locations are within areas of extreme concern. Ecology's SOP EAP070 addresses invasive species transport and contamination and will be followed if any sites for study are identified as having invasive species.

8.4 Equipment decontamination

Section 5.2 Special training and certification lists Ecology's SOP EAP090, *Decontamination of Sampling Equipment for Use in Collecting Toxic Chemical Samples*.

8.5 Sample ID

Sample ID will be maintained throughout the study, using unique identifiers. All soil, sediment, and water samples will be labeled starting with a descriptor of a significant feature of the area, for example, nearest road, water body name, or the name of the nearest city or town. An alpha/numeric identifier will follow the site name starting with the matrix, followed by the transect number from one to five. ID examples:

Transect soil sample ID	Mill-SOIL1 or Mill-SOIL1REP
Transect sediment sample ID	Mill-SED1 or Mill-SED1REP
Water sample ID	Mill-WAT or Mill-WATREP

8.6 Chain-of-custody, if required

Chain-of-custody procedures will be followed throughout the sampling and analytical process. The chain-of-custody will be documented and maintained by use of the laboratory analysis request forms.

8.7 Field log requirements

A field book will be maintained that includes information for all reconnaissance, sample events, and site visits. All field notes including pictures will be maintained by the project lead and archived with other pertinent study information and materials. Information in field books will include but will not be limited to:

- Name and location of project
- Field personnel present
- Date, time, location, ID, and description of each sample
- Weather or other environmental conditions
- Any field measurements or picture identification
- Identity of QC samples collected
- Any changes or deviations from the QAPP

Field notes will be written by permanent waterproof ink on Rite-in-the-Rain paper. Mistakes made in field notes will be corrected by a single line strikethrough with author initials and date.

8.8 Other activities

Dedicated stainless steel bowls and spoons will be used for sub-sampling and homogenizing sediment or soil from each station to a uniform color and consistency. Sediment debris on the sediment surface or materials contacting the sides of the grab sampler will be discarded. Soil samples will be collected using dedicated stainless steel bowls and spoons after loose debris on the soil surface is removed. The top 2 centimeters of soil or sediment will be collected and retained for analysis.

9.0 Measurement Methods

9.1 Field procedures table/field analysis table

The surface water temperature will be determined by red-line alcohol thermometer. The pH will be measured by a HACH field pH meter calibrated just before use, while the specific conductance will be field-measured by a hand-held Hanna conductivity/temperature probe. See Table 7 below for analytical procedures.

9.2 Lab procedures table

Below in Table 8 are the expected range of results, reporting limits, and clean-up and analytical methods proposed for the study.

Table 8. Analytical methods, expected range of results, and detection limits for the study.

Analyte	Matrix	Expected Range of Results	Reporting Limit	Sample Prep Method	Analytical Method
Soil or Sediment					
pp PAHs	Soil or Sed	10 – 100 ug/Kg	1-5 ug/Kg[1]	EPA 3541/3620	EPA 8270 SIM Isotopic Dilution
pp Metals[2]	Soil	0.1 – 100 mg/Kg[3]	0.1 ug/Kg	EPA 3050	EPA 6020A/7471B[4]
TPH-Diesel	Soil or Sed	10 – 100 mg/Kg	50 mg/Kg	Ecology, 1997, Publication No. 97-602	
TOC	Soil or Sed	0 – 10%	0.1%	PSEP-TOC, Combustion NDIR	
Grain Size	Soil or Sed	NA	0.1%	PSEP 1986, Sieve and Pipet	
Water					
pp PAHs	Water	1 – 10 ug/L	0.05 ug/L	EPA 3535	EPA 8270 SIM Isotopic Dilution
pp Metals	Water	0.005 – 10 mg/L	0.1 - 5[4] ug/L	Filter 0.45 um, H_2SO_4 preserve	EPA 200.8/245.1
Hardness as $CaCO_3$	Water	50 – 200 mg/L	0.3 mg/L	H_2SO_4 preserve	SM 2340B
DOC	Water	< 5.0 mg/L	1.0 mg/L	Filter 0.45 um	SM 5310C

[1] ug/Kg is parts per billion.
[2] Soil/sediment metals analyzed as “total recoverable metals”, while water samples will be analyzed as “dissolved metals”.
[3] mg/L is parts per million.
[4] Hg is 0.05 ug/L, EPA 245.1, Hg soil is 0.0036 mg/Kg EPA 7471B ww.

9.2.1 Analyte

See Table 8.

9.2.2 Matrix

See Table 8.

9.2.3 Number of samples

See Table 4.

9.2.4 Expected range of results

See Table 8.

9.2.5 Analytical method

See Table 8.

9.2.6 Sensitivity/Method Detection Limit (MDL)

See Table 8.

9.3 Sample preparation method(s)

See Table 8.

9.4 Special method requirements

NA

9.5 Lab(s) accredited for method(s)

Manchester Environmental Laboratory will conduct the PAH, metals, hardness, and total and dissolved organic carbon analyses for soil, sediment, and water. MEL will also be the lead and manage the contract for Materials Testing and Consulting, Incorporated, to do the grain size analyses. Both laboratories are accredited for their respective analytical procedures.

10.0 Quality Control Procedures

10.1 Table of field and lab quality control required

Table 9 shows a list of field quality control (QC) samples and types to be analyzed for the project. Field QC samples provide an estimate of the total variability of the results−field plus laboratory. Field QC will consist of collection and analysis of replicate samples and blanks. Replicate water samples will be two samples collected one after the other as close to the same time and location as possible. Filter blanks will consist of reagent grade water prepared by MEL and passed through the field filter equipment, placed in a sample container, and returned as other samples to the laboratory for analysis.

Table 9. Field quality control samples.

Analysis	Replicates[1]	Filter Blanks[1]
TOC	10	--
DOC	1	--
Hardness	1	--
Grain Size	10	--
TPH-Dx	8	--
PAHs Soil/Sediment	8	--
PAHs Water	3	--
Metals Soil/Sediment	8	--
Metals Water	3	3

[1] Number represents total QC samples for the study.

All efforts will be made to avoid cross-contamination. Field staff will wear non-talc nitrile gloves throughout the sample collection process. Immediately following collection, samples will be stored in iced coolers, until delivered to MEL.

To minimize field variability from sample collection, field samplers will be familiar with and follow methods for the collection and processing of soil, sediment, and water samples. Additional guidance can be found in the Ecology SOPs. See Section 5.2.

Any equipment used in collection or processing samples will be decontaminated prior to going to the field by washing thoroughly with hot tap water and Liquinox detergent, followed by sequential rinses of 10% nitric acid, de-ionized water, pesticide grade acetone, and finally, pesticide-grade hexane. After decontamination, sampling equipment will be air-dried under a fume hood, covered with aluminum foil, and placed in a new Ziploc bag until used.

Field QC for soil and sediment will be split samples from the composite sample. Water samples will also use split sample and also filter blanks for the dissolved metals samples.

10.2 Corrective action processes

When quality control results fall outside the acceptance criteria established in the Quality Assurance Project Plan for the study, the laboratory analyst for the parameter in question will contact the project manager and discuss the problem and how to proceed. The analytical method will be reviewed to see if suggestions for correction are available. Some situations may require a re-analysis of samples in question, while others may not require action. For instance, some surrogates have generally shown lower recoveries and may be representing a surrogate issue rather than problems with the analysis.

11.0 Data Management Procedures

11.1 Data recording/reporting requirements

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

Case narratives included in the data package from MEL will discuss any problems encountered with the analyses, corrective action taken, changes to the requested analytical method, and a glossary for data qualifiers. Laboratory QC results will also be a part of the data package. This will include results for surrogate recoveries, laboratory duplicates, matrix spikes, and laboratory blanks. The information will be used to evaluate data quality, determine if the MQOs were met, and act as acceptance criteria for project data.

Field and laboratory data for the project will be entered into Ecology’s EIM system. Laboratory data will be downloaded directly into EIM from MEL’s data management system. Data from contract laboratories will be submitted in electronic format for inclusion into the EIM system.

11.2 Laboratory data package requirements

Following completion of the sample analyses, the laboratory will provide a standard deliverable package of results. This will also include all relevant quality control data to the study generated by the laboratory. The data package may also be transmitted in hard copy but is required to be delivered electronically via email.

11.3 Electronic transfer requirements

See 11.2 and 11.5.

11.4 Acceptance criteria for existing data

Ecology has not conducted studies of PAH or metals migration from railroad lines. This will be a baseline study for future comparison. The final report may compare PAH data from this study to other PAH study data listed in EIM.

11.5 EIM/STORET data upload procedures

All data result transmittals from laboratories will be provided in an electronic data deliverable (EDD) format that meets Ecology requirements for loading to EIM.

12.0 Audits and Reports

12.1 Number, frequency, type, and schedule of audits

No audits will take place during the sampling for this project.

12.2 Responsible personnel

NA

12.3 Frequency and distribution of report

Following the conclusion of field sampling for the project, analytical results have been received, and a QA data review is complete, a report will be written describing study findings and how it was conducted. A draft report will be written by the principal investigator following conclusion of all field and laboratory work. The report will include, at a minimum, the following:

- A map showing all sampling locations and any other pertinent features of the study area.
- Coordinates of each sampling site.
- Description of field and laboratory methods.
- Discussion of data quality and the significance of any problems encountered.
- Summary tables of the chemical and physical data.
- Results of toxic contaminants related to available criteria.
- Study results with respect to study goals and objectives.
- Conclusions and recommendations based on study findings.

12.4 Responsibility for reports

The Project Manager/Principal Investigator is responsible for report writing. See Table 2.

13.0 Data Verification

13.1 Field data verification, requirements, and responsibilities

NA

13.2 Lab data verification

Data verification involves examining the data for errors, omissions, and compliance with quality control (QC) acceptance criteria. MEL's SOPs for data reduction, review, and reporting will meet the needs of the project. Data packages, including QC results for analyses conducted by MEL, will be assessed by laboratory staff using the EPA Functional Guidelines for Organic Data Review.

MEL staff will provide a written report of their data review which will include a discussion of whether (1) MQOs were met, (2) proper analytical methods and protocols were followed, (3) calibrations and controls were within limits, and (4) data were consistent, correct, and complete, without errors or omissions.

13.3 Validation requirements, if necessary

NA

14.0 Data Quality (Usability) Assessment

14.1 Process for determining whether project objectives have been met

After the project data have been reviewed and verified, the principal investigator will determine if the data are of sufficient quality to make determinations and decisions for which the study was conducted. The data from the laboratory's QC procedures, as well as results from laboratory control standards and duplicates, will provide information to determine if MQOs have been met, along with an assessment of completeness, representativeness, and comparability. Laboratory and QA staff familiar with assessment of data quality may be consulted. The project final report will discuss data quality and whether the project objectives were met. If limitations in the data are identified, they will be noted.

Some analytes will be reported near the detection capability of the selected methods. MQOs may be difficult to achieve for these results. MEL's SOP for data qualification and best professional judgment will be used in the final determination of whether to accept, reject, or accept the results with qualification. The assessment will be based on a review of laboratory QC results. This will include assessment of laboratory precision, contamination (blanks), accuracy, matrix interferences, and the success of laboratory QC samples meeting MQOs.

14.2 Data analysis and presentation methods

The focus of the study is development of baseline data for future comparison. Only basic data analysis will be conducted for PAH and metals results. Results will be presented as simple graphs showing comparisons of all sites based on similar parameters. Results with applicable water quality criteria will be compared.

14.3 Treatment of non-detects

Laboratory results for the determination of total PAHs, total LPAHs, total HPAHs, and metals in soil, sediment, and water will include detected compounds and “J” qualified results (positively identified, estimated concentration) measured within each sample. There is no total PAH criterion for water but 11 of the 16 pp PAHs do have a criterion and so do 10 of the 13 pp metals. Results that will not be considered a detected analyte or included in sample totals are ”NJ” qualified (tentatively identified, approximate concentration) and non-detected compounds (“U” or “UJ”).

14.4 Sampling design evaluation

The Project Manager/Principal Investigator will be responsible for deciding whether the laboratory data package meet the MQOs established in the QA study plan. The assessment will also determine completeness, representativeness, and comparability along with whether methods allow enough statistical power to draw conclusions for which the study was developed.

14.5 Documentation of assessment

The study report will include a data quality assessment of findings included in the data quality section of the report.

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16.0 Figures

The figures in this QAPP are inserted after they’re first mentioned in the text.

17.0 Tables

The tables in this QAPP are inserted after they're first mentioned in the text.

18.0 Appendix. Glossaries, Acronyms, and Abbreviations

Glossary of General Terms

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

Sediment: Soil and organic matter that is covered with water (for example, river or lake bottom).

Stormwater: The portion of precipitation that does not naturally percolate into the ground or evaporate but instead runs off roads, pavement, and roofs during rainfall or snow melt. Stormwater can also come from hard or saturated grass surfaces such as lawns, pastures, playfields, and from gravel roads and parking lots.

Total Maximum Daily Load (TMDL): A distribution of a substance in a water body designed to protect it from not meeting (exceeding) water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a margin of safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

303(d) list: Section 303(d) of the federal Clean Water Act, requiring Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality-limited estuaries, lakes, and streams that fall short of state surface water quality standards and are not expected to improve within the next two years.

Acronyms and Abbreviations

DOC	Dissolved Organic Carbon
Ecology	Washington State Department of Ecology
e.g.	For example
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
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
NTR	National Toxics Rule
PAH	Polynuclear Aromatic Hydrocarbon
PBT	persistent, bioaccumulative, and toxic substance
QA	Quality assurance

SOP	Standard operating procedures
TOC	Total organic carbon
TSS	Total Suspended Solids
WAC	Washington Administrative Code
WDFW	Washington Department of Fish and Wildlife
WQA	Water Quality Assessment
WRIA	Water Resource Inventory Area

Units of Measurement

°C	degrees centigrade
dw	dry weight
kg	kilogram, a unit of mass equal to 1,000 grams
mm	millimeter, unit of length equal 1/1000 meter
mg	milligram, unit of mass equal to 1/1000 gram
mg/Kg	milligrams per kilogram (parts per million)
mg/L	milligrams per liter (parts per million)
mL	milliliter, unit of volume equal to 1/1000 liter
ug/Kg	micrograms per kilogram (parts per billion)
ug/L	micrograms per liter (parts per billion)

Quality Assurance Glossary

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Examples of data types commonly validated would be:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Split Sample: The term split sample denotes when a discrete sample is further subdivided into portions, usually duplicates. (Kammin, 2010)

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

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

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

References for QA Glossary

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