Quality Assurance Project Plan

6PPD-q in Highway Runoff, BMP Effectiveness, and Field Protocol Development

Prepared for
Washington Department of Ecology

Prepared by
Herrera Environmental Consultants, Inc.

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Science + Planning + Design

Note:
Some pages in this document have been purposely skipped or blank pages inserted so that this document will print correctly when duplexed.

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May 2023

PROJECT TEAM SIGNATURE PAGE

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Published May 2023

Approval signatures indicate that each key member of the project team has reviewed this Quality Assurance Project Plan (QAPP) and agree to follow the methods and quality assurance (QA) procedures contained herein.

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Brandi Lubliner, Ecology Technical Reviewer, Washington State Department of Ecology

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Contents

Appendices

Appendix A	Field Sheets
Appendix B	Chain-of-Custody Form
Appendix C	Ecology Sampling SOP

Tables

Figures

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1. ABSTRACT

6PPD-quinone (6PPD-q) is acutely toxic to coho salmon (*Oncorhynchus kisutch*) and, to a lesser degree, toxic to several other aquatic species. 6PPD-q is a degradation product of a preservative (6PPD) used in automobile tires to extend their lifespan. To protect coho and other aquatic life, environmental managers need more knowledge on the levels of 6PPD-q found in highway runoff and how effective modern stormwater technology is at removing 6PPD-q in stormwater runoff. Additionally, we need to establish best practices for collecting composite stormwater samples for 6PPD-q analysis.

This is an exploratory study effort to (1) inform refinement, if needed, of existing field protocols for collecting stormwater treatment samples for this new parameter 6PPD-q, (2) to collect storm event data to characterize 6PPD-q in runoff in Seattle (Interstate 5) and Portland (Interstate 205) and evaluate the ability of stormwater technologies to reduce 6PPD-q concentrations, and (3) evaluate inter-laboratory differences in reported values of 6PPD-q.

To accomplish the above project goals, we will:

- Analyze 6PPD-q concentrations and assess removal efficiency in 10 paired untreated and treated stormwater runoff samples for each evaluated stormwater technology over the course of five storm events at the Ship Canal Testing Facility in Seattle, Washington. Ten samples of untreated stormwater runoff from five storm events will also be collected from the Stormwater Treatment Technology Center in Portland, Oregon. The untreated samples can be used to characterize stormwater runoff.
- Analyze differences in 6PPD-q concentrations collected through varying field equipment collection techniques from 10 stratified and split samples of untreated stormwater runoff. Further, a set of split samples will also be analyzed by a secondary laboratory to evaluate inter-laboratory differences.

2. BACKGROUND

2.1. Introduction and Problem Statement

This quality assurance project plan (QAPP) describes an exploratory study to characterize 6PPD-q[1] in stormwater runoff. The study will also evaluate removal by stormwater treatment technology, the potential loss of 6PPD-q due to field sampling protocols and equipment, and differences in 6PPD-q quantification between two analytical laboratories. The project is funded by the Washington State Department of Ecology (Ecology). The monitoring project's technical objectives and Ecology's related project requirements are described in this QAPP.

For the past two decades, researchers in the Pacific Northwest of the United States (U.S.) have been studying urban runoff mortality syndrome (URMS) in coho salmon. Years of investigations have sought to identify the chemical(s) causing the mortality in coho (Tian et al. 2020, Tian et al. 2021).

In 2020, researchers identified a chemical in stormwater that forms from an antioxidant used in tires to extend their lifespan. The chemical, 6PPD, upon oxidation becomes 6PPD-q. This chemical is acutely toxic to coho and, to a lesser degree, toxic to several other aquatic species (Tian et al. 2021, 2022; Brinkmann et al. 2022; Hiki et al. 2021). Stormwater has shown acute toxicity for juvenile steelhead and chinook salmon but at lower levels, which may be related to 6PPD-q or other chemicals (French et al. 2022).

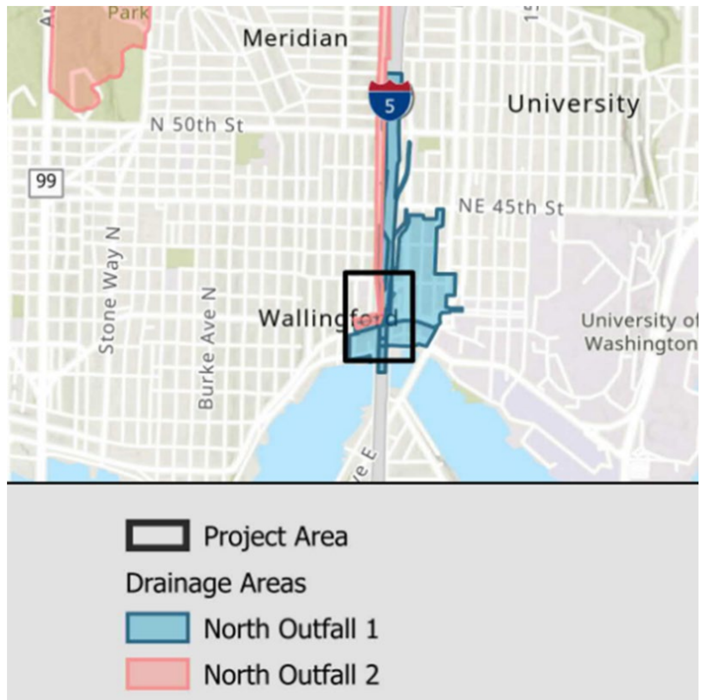
The preferred method of characterizing chemical constituents across the storm event is through the use of flow-weighted sampling. In flow-weighted sampling, flow rate is monitored to trigger collection of aliquots to represent known volumes of water, which generate a composite sample. A common procedure for flow-weighted sampling is the deployment of an automated peristaltic sampler (autosampler). Autosamplers employ a combination of tubing, pump, and carboy. Tubing is placed in the source water, routed through the peristaltic pump, and pumped water is collected in the carboy. Some pollutants can chemically adhere (sorb) to different materials, which may result in a decrease of that chemical in the sample analyzed by the laboratory. The loss of 6PPD-q due to sorption to various field equipment is not yet well-characterized, and completely unevaluated for stormwater sampling protocols. Analysis at University of Washington Tacoma has found sorption to plastic, rubber, and silicone materials (Kolodziej, unpublished data), but the researchers did not accurately model actual field conditions and exposure kinetics.

[1] 2-anilino-5-(4-methylpentan-2-ylamino)cyclohexa-2,5-diene-1,4-dione

2.2. Study Area and Surroundings

Samples will be collected at the Ship Canal Testing Facility (SCTF) in Seattle, Washington, and at the Stormwater Technology Testing Center (STTC) in Portland, Oregon. SCTF is owned by the Washington State Department of Transportation (WSDOT) and is located beneath the I-5 bridge over the Ship Canal (Figure 1). The drainage area contributing to the site is approximately 31.6 acres, with 22.7 acres of pavement and 8.9 acres of landscaping. All runoff in the drainage basin passes through catch basins prior to entering the stormwater collection system and being consolidated in a 30-inch pipe. The drainage basin contains 15 Type 1 and 53 Type 2 catch basins.

WSDOT constructed the SCTF to allow the simultaneous testing of up to four stormwater treatment technologies. This is accomplished by diverting stormwater flow from the 30-inch pipe to the site using a “drawbridge” half-pipe structure and a series of flow splitters. Flow from the draw bridge enters an adjustable flow splitter that diverts water toward test bays 1 and 2 on one side, and toward test bays 3 and 4 on the other side (Figure 2). During this study samples will be collected for treatment technologies located in all four bays.



SCTF drainage area in blue. Seattle, Washington.

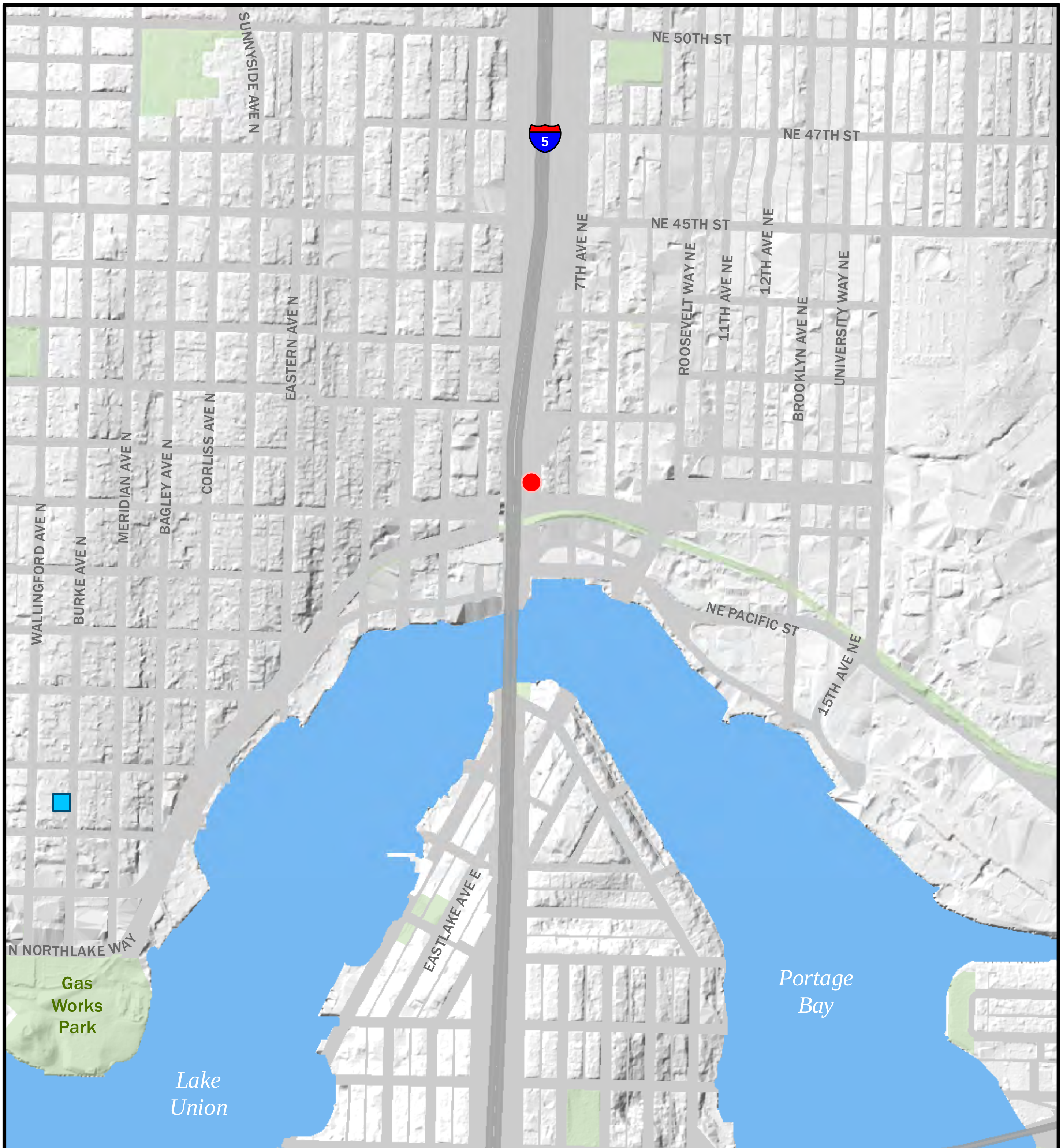


Figure 1.
Site Vicinity Map, WSDOT Ship Canal Test Facility, Seattle, Washington.

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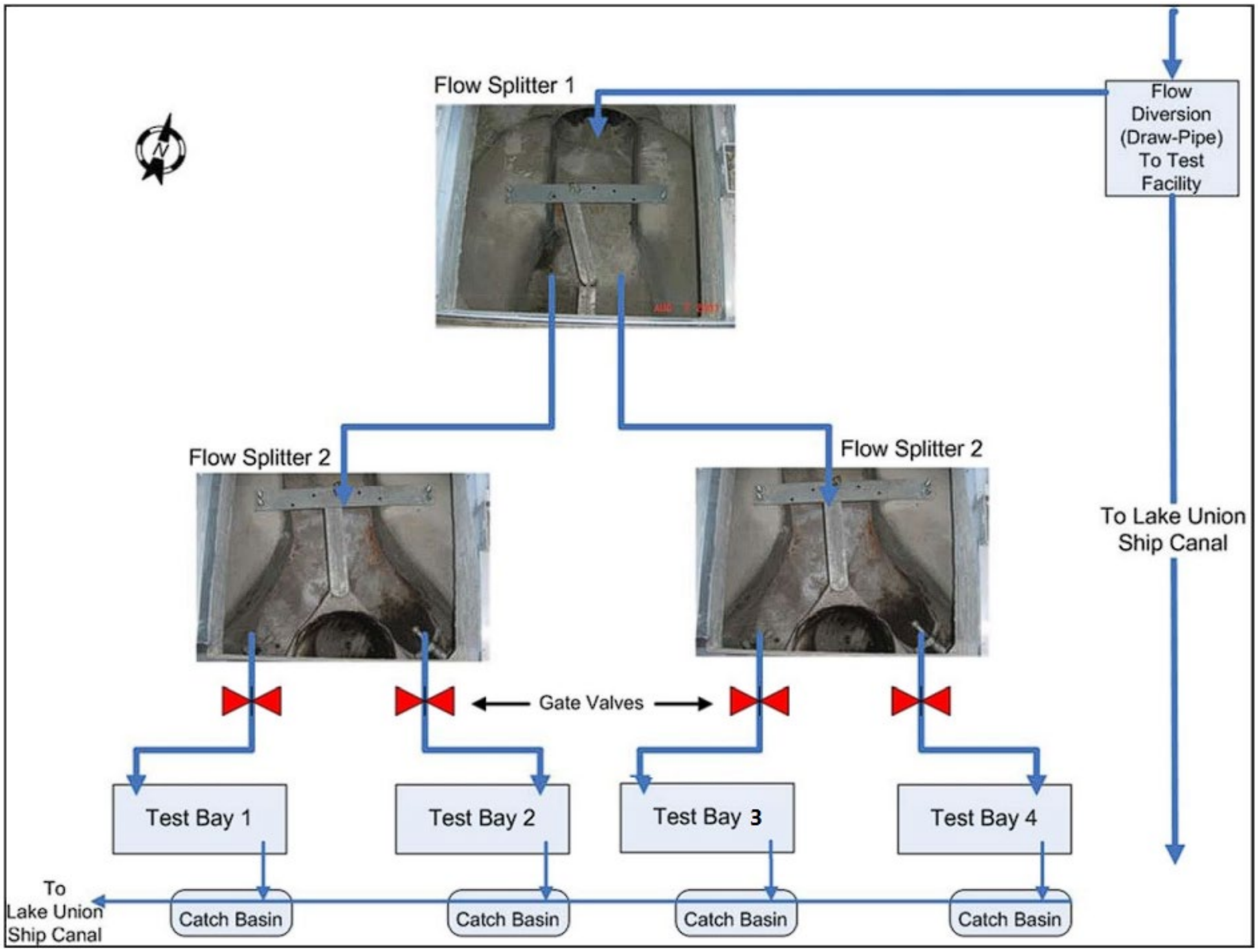

Figure 2. Schematic of the Ship Canal Test Facility Test Bay Configuration and Flow Splitters.

STTC is owned by the Oregon Department of Transportation (ODOT) and is located along I-205. The drainage area contributing to the STTC is approximately 1,000 acres, the majority of which is from I-205 and roadside landscaping with minor contributions from adjacent mixed urban land uses. The facility is located near an 84-inch storm drain that ultimately discharges to the Columbia Slough to the north. Stormwater is diverted from the 84-inch storm drain to a wet well where stormwater is delivered to treatment technologies through air operated double diaphragm pumps. These pumps are controlled by a programmable logic controller and allow delivery of custom hydrographs to test BMPs. In addition, three gravity lines are installed to convey stormwater to the test bays.

In addition to testing treatment performance, the STTC's primary objective is to provide maintenance cycle testing for BMPs. The large volume of stormwater and pump-driven hydrographs can consistently deliver high-intensity storm events to treatment devices over relatively short periods. The mass of suspended sediment delivered to each treatment technology may then be tracked over this period to estimate how frequently maintenance would be required given representative sediment loading rates for typical land uses.

Legend

Site boundary

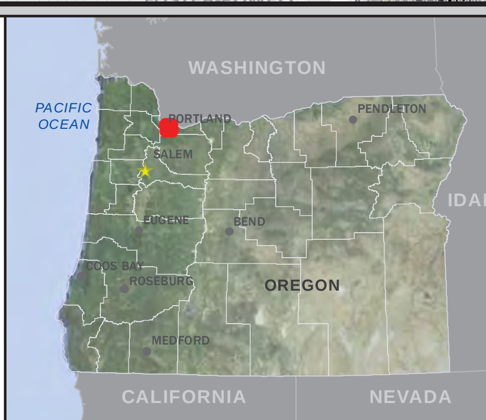

Figure 3.
Vicinity Map for the Oregon Stormwater Treatment Technology Testing Center in Portland, Oregon.

N

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2.2.1. History of Study Area

Not applicable for this study.

2.2.2. Summary of Previous Studies and Existing Data

After identification of 6PPD-q as a primary culprit of URMS in coho salmon, several studies were conducted to characterize concentrations in urban streams and refine sampling and analytical protocols (Tian et al. 2021, 2022; Brinkmann et al. 2022; Hiki et al. 2021).

Published studies documenting 6PPD-q concentrations in stormwater or surface waters are increasing in number but are still limited. Ecology (2022) summarized available 6PPD-q concentration with roadway runoff concentrations ranging from 0.005 to 1.2 µg/L, and urban runoff ranging from 0.021 to 5.5 µg/L (Tian et al. 2021, 2022; Challis et al. 2021; Monaghan et al. 2021; Cao et al. 2022). Additional data are needed to characterize in 6PPD-q in highway runoff and other land uses. In Washington, stormwater treatment technologies (also called best management practices [BMPs]) are reviewed and certified by the State Technology Assessment Protocol–Ecology, better known as the TAPE program. For 6PPD-q, there is need to evaluate of the established field protocol for sampling BMP treatment for this novel parameter to inform future protocol updates.

Recent analysis at the University of Washington–Tacoma (UW Tacoma) Center for Urban Waters found sorption (i.e., loss) of 6PPD-q to PTFE plastic, rubber, and silicone containers over 5 minutes to 24 hours, with greater sorption at 24 hours and for rubber and silicone (Kolodziej, unpublished data). Glass did not exhibit any sorption of 6PPD-q.

2.2.3. Parameters of Interest and Potential Sources

6PPD-q is the primary parameter of interest. 6PPD-q is a degradation product of a preservative (6PPD) used in automobile tires to extend their lifespan (Tian et al. 2021, 2022; Brinkmann et al. 2022; Hiki et al. 2021). Several aquatic species suffer acute toxicity related to 6PPD-q (Table 1).

Table 1. Summary of Toxicity Thresholds from Peer-Reviewed Literature.

Species	LC50 (ug/L)	Source
Brook Trout (*Salvelinus fontinalis*)	0.59 (24 hrs)	Brinkmann et al. 2022
Rainbow Trout (*Oncorhynchus mykiss*)	1.00 (72 hrs)	Brinkmann et al. 2022
Coho (juvenile) (*Oncorhynchus kisutch*)	0.095 (24 hrs)	Tian, 2022
Arctic Char (*Salvelinus alpinus*)	>14.2 (96 hrs)	Brinkmann et al. 2022
White sturgeon (*Acipenser transmontanus*)	>12.7 (96 hrs)	Brinkmann et al. 2022
Zebrafish larvae (*Danio rerio*)	>70 (96 hrs)	Hiki et al. 2021
Japanese medaka (*Oryzias latipes*)	>40 (96 hrs)	Hiki et al. 2021
Daphnia magna	>60 (40 hrs)	Hiki et al. 2021
Hyalella azteca	>90 (96 hrs)	Hiki et al. 2021

Sources of 6PPD-q to the environment are expected to be primarily from tires. The parent compound, 6PPD, from which 6PPD-q is derived by reaction with ozone, is recommended for use as an anti-ozonant in the tread, sidewall, and rim strip of tires, as well as the rubber cover of conveyor belts (Sheridan 2010). All tires produced by the 12 member companies of the U.S. Tire Manufacturers Association use 6PPD as the primary antiozonant <https://www.ustires.org/6ppd-and-tire-manufacturing>. Tires stored uncovered outdoors and re-uses of tires such as crumb rubber in synthetic turf, playgrounds, and incorporation into materials such as rubberized asphalt may continue to contribute 6PPD-q to the environment, but direct investigation is required for confirmation.

Rubbers used as seals may also contain 6PPD, depending on the ozone resistance of the elastomer (Sheridan 2010). For example, whereas ethylene-propylene rubbers (EPM or EPDM) are resistant to ozone, and isobutylene-based elastomers and neoprenes are moderately resistant, natural rubber, styrene-butadiene, polybutadiene, and nitrile elastomers readily degrade in the presence of ozone and require an anti-ozonant such as 6PPD to protect the rubber from cracking as it ages (Sheridan 2010).

2.2.4. Regulatory Criteria or Standards

Not applicable.

2.3. Water Quality Impairment Studies

Not applicable.

2.4. Effectiveness Monitoring Studies

Not applicable.

3. PROJECT DESCRIPTION

This QAPP outlines the steps the Project Team intends to take to meet the goals and objectives described below and provide data to Ecology. It includes data quality objectives (DQOs), method quality objectives (MQOs), study design, experimental procedures, and plans for quality control and data management. This project will analyze individual grab samples for 6PPD-q. Quality assurance of the data will be evaluated prior to June 30, 2023, to gain insights on the behavior and concentration profile of 6PPD-q. From this work, Ecology expects to gain a better understanding of 6PPD-q levels in runoff, removal rates by modern stormwater technologies, and if existing field protocols for treatment evaluations of stormwater will need to be modified due to 6PPD-q loss to materials.

There is considerable interest in evaluating whether automated sampling of stormwater results in any loss of 6PPD-q through degradation or sorption to sampling materials. In automated sampling, numerous aliquots of source water are pumped via tubing to a carboy. The sampled water in the carboy is later delivered to a laboratory, homogenized, and split into various bottles for analysis for select chemical parameters.

For the collection of aliquots, a suction line (typically PTFE [polytetrafluoroethylene – Teflon®] or vinyl) is placed in source water and pumped using vacuum suction or peristaltic pumping. If using a peristaltic pump, the suction line is attached to a silicone tube within the peristaltic pump head because silicone has the necessary elasticity for optimal pump performance. The suction line material may provide sorption potential for 6PPD-q. Silicone and vinyl tubing are specifically of concern. PTFE-lined tubing is theorized to provide less sorption potential. The silicone tubing perturbation by peristaltic pumping may increase sorption. This study will vary tubing material to evaluate 6PPD-q loss.

Pumped aliquots are deposited in a carboy over the course of the storm. The carboy material is typically HDPE (high density polyethylene), glass, or FLPE (fluorinated high-density polyethylene). The carboy material may provide sorption potential for 6PPD-q. Loss via sorption to HDPE carboys is expected to increase with time. Sorption to glass is not anticipated. This study will vary the time-of-exposure to HDPE and FLPE material.

Additionally, this study will compare the analytical results from the King County Environmental Laboratory (KCEL) and the Manchester Environmental Laboratory (MEL) for split stormwater runoff samples.

3.1. Project Goals

The project goals are:

- to collect data that can inform refinement of a field protocol for collecting stormwater samples for 6PPD-q analysis
- to collect storm event data to characterize 6PPD-q in stormwater runoff in Seattle, Washington (I-5) and Portland, Oregon (I-205)
- to evaluate the ability of stormwater technologies to reduce 6PPD-q concentrations
- to evaluate inter-laboratory differences in reported values of 6PPD-q

3.2. Project Objectives

To accomplish the above project goals, we will:

- Analyze 6PPD-q concentrations and assess removal efficiency in 10 paired untreated and treated runoff samples for each evaluated stormwater technology over the course of five storm events at the SCTF. Ten samples of untreated stormwater runoff from five storm events will also be collected from the STTC. The untreated samples can be used to characterize stormwater runoff.
- Analyze differences in 6PPD-q concentrations collected through varying field equipment exposures from 10 stratified and split samples of untreated stormwater. These include:
  - Direct to amber glass bottle (and field duplicate)
  - Tubing material (silicone, PTFE [Teflon])
  - FLPE bottle material exposure times
  - HDPE bottle material exposure times
- Analyze differences in in 6PPD-q concentrations reported by KCEL and MEL for 10 replicates of untreated runoff.

3.3. Information Needed and Sources

To meet the project objectives, we will rely on data collected in this study, both field notes and reported laboratory values.

3.4. Tasks Required

Tasks required:

- Track upcoming storms that meet criteria.
- Coordinate with laboratories to ensure capacity to analyze incoming samples.
- Collect grab samples of untreated and treated stormwater runoff for each stormwater technology twice during each of five storms at the SCTF.
- Collect grab samples of untreated stormwater runoff twice during each of five storms at the STTC.
- Use a churn splitter to collect and distribute homogenized untreated runoff (10 collections) through various sampling protocols.
- Deliver samples to analytical labs within holding times.
- Review analytical data and perform statistical analysis.

3.5. Systematic Planning Process

Not applicable.

4. ORGANIZATION AND SCHEDULE

4.1. Key Individuals and Their Responsibilities

Table 2 shows the responsibilities of those who will be involved in this project.

Table 2. Organization of Project Team.

Staff	Title	Responsibilities
Brandi Lubliner Washington Department of Ecology Phone: 360-407-7140	Ecology Reviewer	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.
Morgan Baker Washington Department of Ecology Phone: 360-706-4079	Ecology Project Manager	Clarifies scope of the project and coordinates with MEL and TAPE staff. Provides internal review of the QAPP and approves the final QAPP.
Timothy Clark Herrera Environmental Consultants, Inc. Phone: 971-361-2238	Project Manager	Writes the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data and analyzes and interprets data. Writes the draft report and final report.
Dylan Ahearn Herrera Environmental Consultants, Inc. Phone: 206-787-8290	Principal Investigator Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Nicholas Harris Herrera Environmental Consultants, Inc. Phone: 206-787-8311	Field and Technical Assistant	Helps collect samples and records field information. Supports QA review of data, and analyzes and interprets.
Sam Nilsson Herrera Environmental Consultants, Inc. Phone: 971-200-8871		
Meghan Elkey King County Environmental Laboratory Phone: 206-477-7154	Lab Project Manager	Reviews draft QAPP, coordinates with Project Manager.
Francis Sweeney King County Environmental Laboratory Phone: 206-477-7117	Lab Supervisor	Supervises laboratory analysis.
Joan Protasio Manchester Environmental Lab Phone: 360-871-8824	Organics Supervisor	Supervise laboratory analysis.

QAPP: Quality Assurance Project Plan

4.2. Special Training and Certifications

Field staff have been trained and are experienced in storm and TAPE sampling procedures, including the use of peristaltic pumps, handling sampling equipment to prevent contamination, and properly transporting sample bottles. Laboratory staff are highly specialized in the applicable equipment. No additional training or certifications are needed for staff this study.

Field staff have been vetted and granted access to both the SCTF and STTC from the managing entities. SCTF is owned by WSDOT and managed by Ecology. STTC is owned by ODOT and managed by Herrera.

4.3. Organization Chart

Not applicable. See Table 2.

4.4. Proposed Project Schedule

Table 3 lists key activities, due dates, and lead staff for this project.

Table 3. Proposed Schedule for Completing Field and Laboratory Work, Data Management, and Reports.

Field and Laboratory Work	Due Date	Lead Staff
Field work	June 2023	Nicholas Harris and Sam Nilsson
Laboratory analyses	July 2023	Meghan Elkey
Data Management and Analysis		
Data Uploaded and QC'd	August 2023	Nicholas Harris and Sam Nilsson
Statistical Analysis	October 2023	Timothy Clark
Final Report and Field Protocol Recommendation Memo		
Author Lead / Support Staff	Timothy Clark / Sam Nilsson	
Schedule		
Internal draft	Early November 2023	
Draft to client	Late November 2023	
Final report to client	December 2023	

4.5. Budget and Funding

The project is funded through a proviso passed in Engrossed Substitute Senate Bill 5092, Section 302 (23) to the Washington State Department of Ecology.

The number of samples analyzed by King County Environmental Laboratory and Manchester Environmental Laboratory are summarized in Table 4 below.

Table 4. Summary of the Number of Laboratory Samples.

Study Component	Receiving Laboratory	Samples per Event	Number of Events	Total Number of Samples
SCTF Highway and BMP Evaluation	KCEL	13	5	65
STTC Highway and BMP Evaluation	KCEL	2 or 3[a]	5	11
Field Protocol Evaluation	KCEL	80	1	80
	MEL	10	1	10

[a] A field duplicate will be collected at the STTC for sampling event 2.

5. QUALITY OBJECTIVES

5.1. Data Quality Objectives

The goal of this QAPP is to ensure that the data collected for the field protocol evaluation and stormwater runoff 6PPD-q characterization are scientifically accurate, useful for the intended analysis, and defensible. To achieve this goal, the collected data will be evaluated relative to the measurement quality objectives described in the following sections.

5.2. Measurement Quality Objectives

Measurement quality objectives (MQOs) in this section establish the performance metrics and criteria for acceptance that provide the basis for evaluating data quality and usability.

5.2.1. Targets for Precision, Bias, and Sensitivity

MQOs for precision, bias, and sensitivity are the method performance metrics and criteria for acceptance that provide the basis for evaluating data quality and usability are described below in Table 5.

Table 5. Measurement Quality Objectives (e.g., for laboratory analyses of water samples).

Parameter	Reporting Limit	Method Detection Limit	Method Blank	Rinsate Blank	Laboratory or Field Duplicate RPD or Difference[a]	Matrix Spike Percent Recovery	Spike Blank Percent Recovery
6PPD-quinone (KCEL)	0.05 µg/L	0.01 µg/L	<MDL	<RL	40% or ± 2 × RL	50-150	50-150
6PPD-quinone (MEL)	0.001 µg/L	0.000365 µg/L	<1/2 RL	<RL	40	40-160	50-150

[a] The relative percent difference must be less than or equal to the indicated percentage for values greater than five times the reporting limit. The absolute difference must be less than or equal to two times the reporting limit for values less than or equal to five times the reporting limit.

KCEL – King County Environmental Laboratory

RPD = relative percent difference

MDL = method detection limit

MEL – Manchester Environmental Laboratory

RL = reporting limit

µg/L = micrograms per liter

Precision

Precision is a measure of the repeatability of a set of replicated results and represents random error in the measurement process. Targets for acceptable precision in terms of relative percent difference (RPD) are presented in Table 5 above.

Bias

Bias is the systematic or persistent distortion of a measurement process which makes the result non-representative of the true value that can come from field sampling or laboratory sample handling. Errors of field bias are minimized through field training and following standard procedures. Errors of bias in laboratory analytical measurements are minimized through use of standardized procedures by properly trained staff. Analytical bias will be assessed through the analysis of method blanks, rinsate blanks, matrix spikes, and laboratory control samples (Table 5).

Sensitivity

Sensitivity is measured through reporting limit performance (for example, in a regulatory setting, the method detection limit [MDL] is often used to describe sensitivity). MDLs and reporting limits will be provided with each analytical data report. Target MDLs and reporting limits are presented in Table 5. above.

5.2.2. Targets for Comparability, Representativeness, and Completeness

These categories of MQO—representativeness, comparability, and completeness—inform whether the project will generate data that can be interpreted as planned. Potential sources of interference with these MQOs include sampling and analytical procedures that introduce contamination, loss (e.g., sorption) of targeted analytes to experimental equipment, transformation of target analytes in samples during transportation and storage, interference from other constituents in the sample matrix, inability of the analytical method to measure all forms of the constituent of interest, and absent or faulty instrument calibration. Inconsistent performance or not adhering to SOPs impacts comparability.

5.2.2.1. Comparability

Analytical results may be used in comparisons to, (1) each other, among samples collected for this study, (2) results of similar surveys reported in the past or future by other local agencies or in peer reviewed literature, (3) results of future surveys by King County or Ecology, and (4) results of studies that document impacts of 6PPD-q field protocols. The primary means to ensure the project meets these comparability requirements is through the use of SOPs and standard methods. Analytical methods to be employed during the project are described in Section 8. SOPs utilized in this project are listed below and provided in Appendix C.

- Collecting Grab Samples from Stormwater Discharges SOP version 1.1

Modifications to this sampling SOP are described in detail in Section 7.2.

5.2.2.2. Representativeness

The sampling to be conducted for this project will generate stormwater 6PPD-q data representing discharge of roadway runoff gathered at two routinely used stormwater testing facilities and 6PPD-q reduction performance data for multiple high flow stormwater media filters. Storm events will be targeted that coincide with sampling events for performance monitoring of the selected BMPs following Ecology's Technology Assessment Protocol–Ecology (TAPE) guidelines (Ecology 2018). The following criteria will serve as guidelines for defining the acceptability of specific storm events for sampling. These criteria are identical to the storm criteria listed in the BMP monitoring QAPPs.

- Target storm depth: a minimum of 0.15 inch of precipitation over a 24-hour period.
- Antecedent conditions: a period of at least 6 hours preceding the event with less than 0.04 inch of precipitation.
- Minimum duration: target storms must have a duration of at least 1 hour.

If feasible, field staff will attempt to target a range of rainfall intensities for the BMP evaluation and stormwater runoff characterization components of this study.

5.2.2.3. Completeness

For this study to be successful, stormwater runoff at the designated sampling locations from five discrete storms will be collected. Samples will be collected for BMP evaluation from five qualifying storms and for field protocol sampling from one qualifying storm. At least 90 percent of BMP evaluation samples must be successful, and at least 9 of 10 sample sets in the field protocol sampling must be successful.

5.3. Acceptance Criteria for Quality of Existing Data

Not applicable.

5.4. Model Quality Objectives

Not applicable.

6. STUDY DESIGN

6.1. Study Boundaries

Water quality sampling will take place at the SCTF in Seattle, Washington and STTC in Portland, Oregon. The SCTF and STTC are described in Section 2.2. This study is specific to analysis of 6PPD-q. Additional flow-weighted composites and grab sampling may coincidentally be collected during the targeted storm events as part of other monitoring projects. It is not in the scope of this study to assess correlations with those samples or hydrologic information.

6.2. Field Data Collection

For all study components, sampling will be targeted toward wet-weather events with the following characteristics:

- Target storm depth: a minimum of 0.15 inch of precipitation over a 24-hour period.
- Antecedent conditions: a period of at least 6 hours preceding the event with less than 0.04 inch of precipitation.
- Minimum duration: target storms must have a duration of at least 1 hour.

Field staff will routinely review meteorological forecasts to identify storms that will meet the above identified characteristics. In communication with Herrera and laboratory project managers, a go/no go decision will be made.

6.2.1. Sampling Locations and Frequency

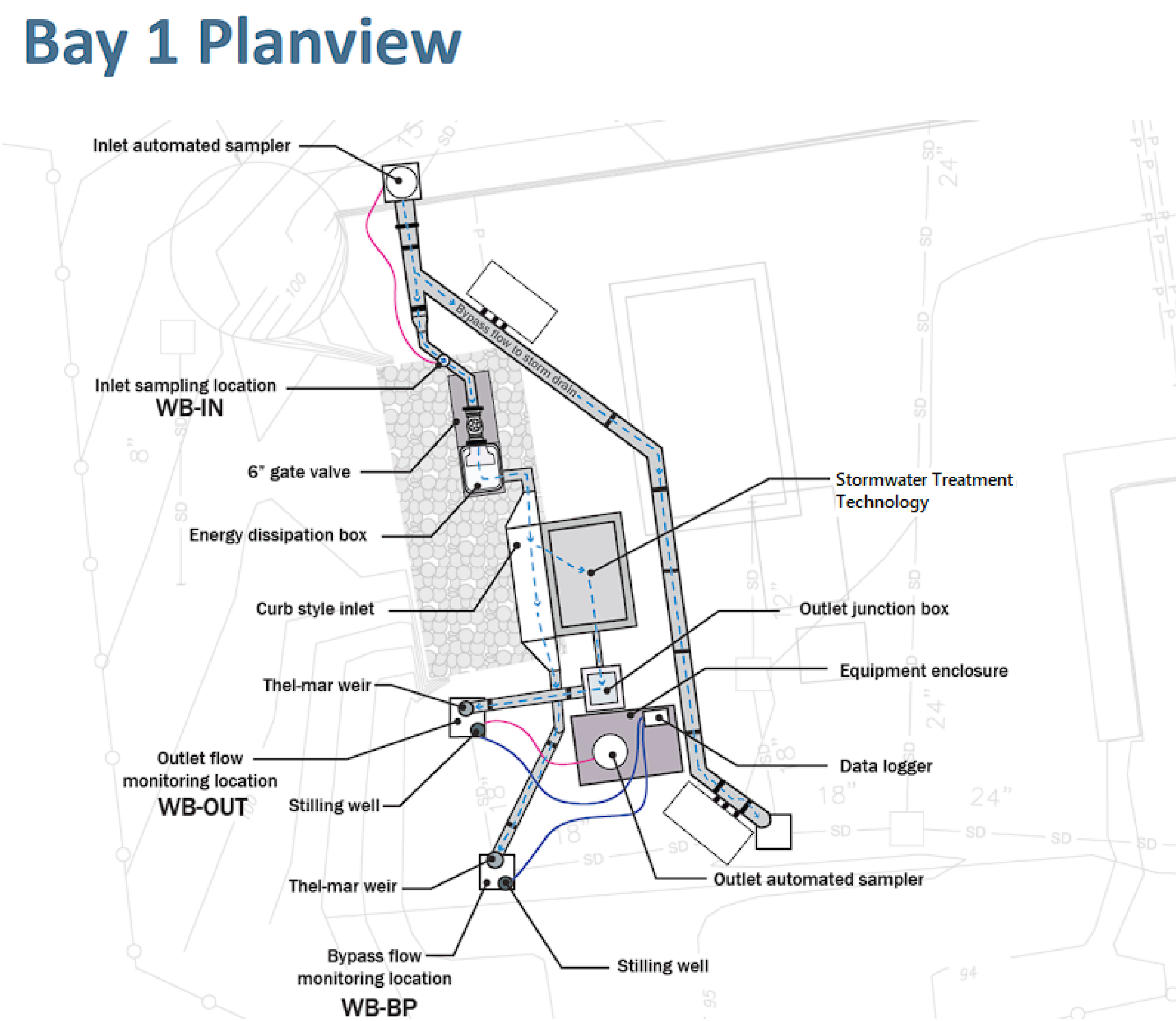
Highway Runoff Characterization and BMP Assessment

At the installed test units at the SCTF, water quality grab samples will be collected from the untreated test unit influent and treated test unit effluent. The upstream sampling station will be designated as [Facility]-[TestBay#]-IN (e.g., SCTF-TB1-IN). The downstream sampling station will be designated as [Facility]-[TestBay#]-IN (e.g., SCTF-TB1-OUT). Water quality grab samples will be collected at the STTC from untreated flow through the facility's central gravity line designated STTC-G2. During each wet-weather event, samples will be collected approximately two to three hours apart. Figures 4 and 5 below detail an example BMP configuration installed at the SCTF and an overview of the STTC layout, respectively.

Table 6 below describes the stormwater technologies that will be monitored at the SCTF. Manufacturers have granted permission for 6PPD-q effluent samples with the understanding that their product name will not be shared in the presentation of the data.

Table 6. Description of Stormwater Technologies Monitored.		
Sampling Station	**Type of Stormwater Technology**	**Hydraulic Loading Rate (gpm/ft²)**
SCTF-TB2	Membrane filter	1.0
SCTF-TB2.5	Horizontal bed media filter	7.1
SCTF-TB4	Cartridge-based media filter	1.5

Figure 4. Example SCTF Bay 1 BMP Configuration.



Field Protocol Evaluation

During a single wet-weather event, untreated stormwater runoff will be collected in a churn splitter, homogenized, and split into various samples (see Table 7). Over the course of the storm, 10 collections and splits will occur. The churn splitter will be field rinsed three-times with source water prior to filling. The collections will be separated by approximately 15 minutes each. The bottles will be filled in the order described in Table 7.

For this study component, we will examine paired differences between each of the split samples and the control for the same churn splitter collection. Additionally, we will look for trends in those difference over time for the carboy and tubing groups, because those material will be reused between churn splitter collections. If 6PPD-q is sorbed to the material, we may expect that the loss coefficient lessens with each sample as sorption area is saturated. The tubing will be purged with DI water between sample sets. The tubing will then be purged with source water. Rinsate blanks will be taken for both tubing experimental groups before sampling commences and after the last sample is collected.

Table 7. Experimental Groups for Field Protocol Development.

Group Code	Description	Purpose	Sampling Priority
CONT	Control sample Amber glass bottle filled directly from churn splitter	Control	1
PTFE_TUB	PTFE tubing PTFE tubing (10-feet) attached to silicone tubing (1-foot) within a peristaltic pump will be used to extract water from the churn splitter to fill sample bottle	Evaluate 6PPD-q loss due to use of a PTFE-to-Silicone tubing and peristaltic pump sampling method.	2
SILI_TUB	Silicone tubing Silicone tubing (2-feet) within a peristaltic pump will be used to extract water from the churn splitter to fill sample bottle	Evaluate 6PPD-q loss due to use of a silicone tubing and peristaltic pump sampling method	3
HDPE_FT	HDPE bottle sample Bottle filled directly from churn splitter, held in bottle until analysis.	Evaluate 6PPD-q loss due to sorption to HDPE	4
HDPE_24	HDPE “carboy” sample Bottle filled directly from churn splitter, held in bottle for 24 hours prior to transfer to amber glass bottle at laboratory.	Emulate typical HDPE exposure time for composite sampling and evaluate 6PPD-q loss due to sorption to HDPE.	5
FLPE_FT	FLPE bottle sample Bottle filled directly from churn splitter, FLPE in bottle until analysis.	Evaluate 6PPD-q loss due to sorption to FLPE	6
FLPE_24	FLPE “carboy” sample Bottle filled directly from churn splitter, held in bottle for 24 hours prior to transfer to amber gloss bottle at laboratory.	Emulate typical FLPE exposure time for composite sampling and evaluate 6PPD-q loss due to sorption to FLPE.	7
LAB	Laboratory split Bottle filled directly from churn splitter and transported to a separate laboratory	Evaluate 6PPD-q reporting differences between two analytical laboratories.	8
FD	Field duplicate sample of control sample Amber glass bottle filled directly from churn splitter	Evaluate 6PPD-q variability in consideration of churn splitter homogenization and lab measurement variability.	9

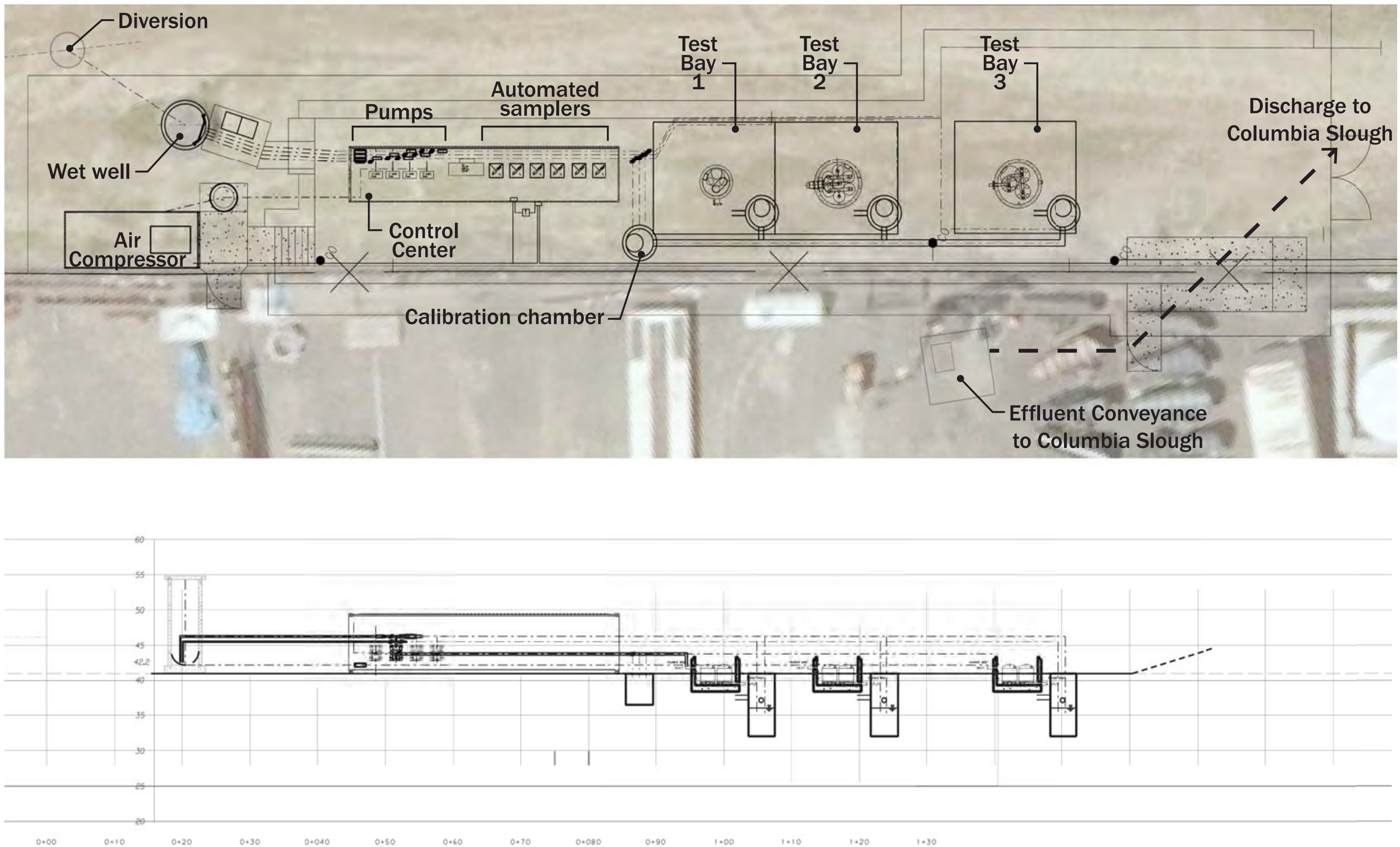


Figure 5.
Plan and Profile View of Major Physical Components for the Oregon Stormwater Treatment Technology Testing Center.

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6.2.2. Field Parameters and Laboratory Analytes to be Measured

6PPD-q will be analyzed for all stormwater samples collected as part of this study.

6.3. Modeling and Analysis Design

Not applicable.

6.4. Assumptions of Study Design

For the highway runoff characterization and BMP evaluation component, the study design assumes that the paired influent and effluent grab samples are representative of the same unit of water that experienced treatment.

For the field protocol evaluation, the study design assumes that the churn splitter will suitably homogenize the collected stormwater.

6.5. Possible Challenges and Contingencies

The monitoring locations proposed for this project were designed for collecting automated and grab stormwater samples and minimize many of the typical issues with these methods. However, potential challenges are discussed in the sections below.

6.5.1. Logistical Problems

Due to uncertainties in weather conditions, grab stormwater sampling can pose a substantial challenge. Primary potential logistical problems are detailed below.

- Storm timing. Timing when to travel to a site to collect stormwater grab samples is challenging and the lag between forecast updates and mobilization time may lead to false starts or missed events. For BMP and highway runoff characterization sampling, two sets of samples will be collected during different phases of each storm. Determining the timing to sample the peak or falling limb or a storm may be challenging for field staff. For field protocol sampling, 10 sets of samples will be collected in a row. If an unanticipated break in the storm occurs, stormwater flow may fall below sampleable levels before all 10 sets of samples are collected.
- Dry season. The project schedule in this QAPP proposes completion of field sampling in June 2023. Extended periods of dry weather may occur which would delay the overall project schedule and require additional sampling at the start of the next wet season. Delays in early planning phases of this project including QAPP review and approval may exacerbate this potential issue.

Risk of encountering logistical problems will be reduced by assigning sampling staff to this project who are experienced in stormwater grab sampling and storm tracking and adhering to storm sampling criteria to reduce frequency of false starts or missed storms. The SCTF location is ideal for grab sampling because of the large contributing area resulting in a long falling limb which decreases likelihood of abandoned events due to low flow.

6.5.2. Practical Constraints

Limited numbers of qualified field samplers are the primary practical constraint for field data collection. This is partly mitigated from the number of other active studies located at the SCTF making it a high field priority location during storm events.

The SCTF and STTC are both private access and require permission to enter. The SCTF is owned by WSDOT and managed by Ecology, and the STTC is owned by ODOT and managed by Herrera. Permission has been attained from these entities for this study. Furthermore, permission has been attained from the BMP manufacturers at the SCTF to obtain effluent samples from their treatment systems.

6.5.3. Schedule Limitations

Potential challenges detailed above may delay the proposed field data collection schedule and in turn delay final data analysis and reporting schedules. This is partly accounted for in the project schedule as additional samples may be collected in Fall 2023, if necessary. Risk of schedule delay is partly limited because grab sampling activities are already underway for different monitoring projects at the SCTF, so mobilization times are expected to be minimal.

7. FIELD PROCEDURES

7.1. Invasive Species Evaluation

Not applicable.

7.2. Measurement and Sampling Procedures

Field sampling procedures for both BMP and field protocol evaluation will generally be consistent with Ecology's SOP *Collecting Grab Samples from Stormwater Discharge* (Appendix C). All samples will be collected from stormwater BMP influent and effluent streams at pre-defined representative locations. Modifications to the SOP are described in detail in the following subsections.

Field staff will routinely review meteorological forecasts to identify storms that will meet the above identified characteristics. Field Samplers will notify KCEL and the Ecology project manager staff upon identification of a target storm event and will attempt to give at least 48 hours of notice prior to collecting samples. Sampling events with less than 48 hours must be confirmed by KCEL staff prior to sample collection.

7.2.1. Highway Runoff and BMP Evaluation Procedures

The following procedures will be used to collect stormwater grab samples at the SCTF:

- To collect the inlet sample, dip the bottle into the pipe at the entry point of each BMP and collect samples as specified in the Ecology SOP. If grab sample ports are installed (SCTF Bay 3), open the sample port and allow stormwater to flow for at least 10 seconds to clear any settled solids.
- To collect the treated outlet sample, place the open bottle beneath the water as it spills over the outlet weir for each BMP and collect samples as specified in the Ecology SOP.
- Field duplicate sample volume will be collected immediately after the sample volume.

The following procedures will be used to collect stormwater grab samples at the STTC:

- Open all three gravity line ball valves and allow stormwater to flow through the wet well system for at least 10 minutes to clear any settled solids in the wet well or lines.
- Dip the sample bottle into the stormwater flow at the end of the central gravity line (G2) hose where it is discharging into the effluent basin as specified in the Ecology SOP.
- Field duplicate sample volume will be collected immediately after the sample volume.

7.2.2. Field Protocol Evaluation Procedures

- Rinse both segments of tubing by backflushing five liters of lab-provided DI water through them using the automated sampler. Collect one pre-sample rinsate blank from each segment of tubing using the automated sampler.
- Place the churn splitter directly in the stream of stormwater and collect the full sample volume required directly into the churn splitter. Full volume is typically 13 liters for 14-liter splitters, and 7 liters for 8-liter splitters. If the samples are collected from a Test Bay with grab sample ports installed, open the port and allow stormwater to flow for at least 10 seconds to clear any settled solids prior to sampling.
- Place the churn splitter on a clean and level surface and insert the churn paddle into the splitter. Ensure there is sufficient clearance beneath the churn splitter sample port to fill sample bottles.
- Pre-mix the sample volume prior to collection of sample bottles by smoothly raising and lowering the churn paddle at a rate of approximately nine inches per second at least ten times. The churn paddle should reach the bottom of the splitter each stroke but should not break the surface of the water. Note that as sample bottles are filled, the volume remaining in the splitter will decrease and the churn stroke length must decrease to prevent breaking the water surface.
- Fill the sample bottles while consistently churning the sample volume. The bottles will be filled in the order described in Table 7. For the two tubing experimental groups, one end of the tubing segment will be placed into the churn splitter and a peristaltic autosampler will be used to fill the sample bottle.
- Upon collection of each set of samples, rinse the churn splitter with at least three times the target sample volume of source water and repeat the previous steps until all sample sets are collected.
- Upon collection of all 10 sets of samples and while it is still wet, rinse the churn splitter with DI water and return it to the laboratory for decontamination.
- Rinse both segments of tubing by backflushing five liters of lab-provided DI water through them using the automated sampler. Collect one post-sample rinsate blank from each segment of tubing using the automated sampler.

7.3. Containers, Preservation Methods, Holding Times

Table 8 presents the sample containers, preservation, and holding times. Additionally, the HDPE_24 and FLPE_24 sample groups will be transferred from their respective 250 mL HDPE and FLPE containers after 24 hours into a 250 mL amber glass container. The transfer will be via hand-pouring.

Table 8. Sample Containers, Preservation, and Holding Times.					
Parameter	**Matrix**	**Minimum Quantity Required**	**Container**	**Preservative**	**Holding Time**
6PPD-quinone (Most samples)	Stormwater	250 mL	250 mL amber glass	4°C (wet ice) in dark. Minimize head space, do not freeze	4 weeks
6PPD-quinone (FLPE "carboy" group)	Stormwater	250 mL	250 mL FLPE	4°C (wet ice) in dark. Minimize head space, do not freeze	4 weeks
6PPD-quinone (HDPE "carboy" group)	Stormwater	250 mL	250 mL HDPE	4°C (wet ice) in dark. Minimize head space, do not freeze	4 weeks

7.4. Equipment Decontamination

Between sample collections, equipment will be rinsed with source and/or deionized water per Ecology's SOP EAP090, Decontamination of Sampling Equipment for Use in Collecting Toxic Chemical Samples. After decontamination, equipment should be handled only by personnel wearing clean gloves to prevent re-contamination. If equipment is not immediately re-used, it should be covered with plastic sheeting, wrapped in aluminum foil, or placed in a labeled resealable plastic bag to prevent recontamination.

7.5. Sample ID

Samples IDs will be generated based on the study component and relevant information. For the highway runoff characterization and BMP assessment samples, the ID will be structured as follows: HR_[DATE]_[IN/OUT]_[TB#]_[GRAB #], where [DATE] is the date of the sample in YYYYMMDD format, [IN/OUT] is IN or OUT for untreated runoff and treated runoff, respectively, [TB#] is the treatment bay number sampled (or STTC for the samples located at the Stormwater Technology Treatment Center), and [GRAB #] signifies if it is the first ("_1") or second ("_2") grab of the storm.

For the equipment and laboratory study samples, the ID will be structured as follows: EQUIP_[GROUP]_[GRAB #], where [GROUP] is the assessment group, and [GRAB #] signifies when the order that the sample was collected. For this study component, [GRAB #] will range from 1 to 10.

QA samples (field duplicates and blanks) will only be labeled as QA1, QA2, etc., for delivery to lab, but field staff will maintain a cross-check list of which stations and sample types the QA samples represent. When results are returned from the laboratory, project staff will associate full label information with the results and populate database fields for QA sample and type.

Waterproof labels will be placed on dry sample container lids by self-adhesion or with tape. Waterproof labeling tape may be employed. Any written marks will be made with waterproof ink.

7.6. Chain of Custody

The primary objective of chain-of-custody procedures is to provide an accurate written or computerized record that can be used to trace the possession and handling of a sample from collection to completion of all required analyses. A sample is in custody when any of the following conditions are true:

- The sample is in someone's physical possession
- The sample is in someone's view
- The sample is locked up
- The sample is kept in a secured area that is restricted to authorized personnel

A chain-of-custody form will accompany each set of samples. The chain-of-custody form (see Appendix B) indicates the name of the collector of the samples, date and time of collection, number of containers, tests to be performed, shipper, receiver, and date and time of shipping and receiving. Samples are to be placed on ice and delivered to the lab according to procedures prearranged with the lab (i.e., courier pickup for SCTF samples or shipped overnight for STTC samples).

The sampler will use the following guidance to ensure proper control of samples while in the field:

- As few people as possible will handle the samples.
- The Field Sampler will be responsible for the care and custody of collected samples until they are transferred to another person or dispatched properly under chain-of-custody rules.
- The Field Sampler will record sample data on standardized field data forms (see example in Appendix B).
- The Field Sampler will determine whether proper custody procedures were followed during the fieldwork and will decide if additional samples are required.
- The Field Sampler will be responsible for packaging samples, mailing or delivering samples to appropriate laboratories, and coordinating pick up with couriers. When transferring custody (i.e., releasing samples to a courier or mailing to a laboratory), the following rules will apply:
    - The container in which samples are packed will be sealed and accompanied by one copy of the chain-of-custody record. When transferring samples, the individuals relinquishing and receiving them must sign, date, and note the time on the chain-of-custody record. This record will document sample custody transfer.
    - Samples will be dispatched to the laboratory for analysis with separate chain-of-custody records accompanying each shipment. Shipping containers will be sealed with custody seals for shipment to the laboratory. The chain-of-custody records will be signed by the relinquishing individual, and the method of shipment, name of courier, and other pertinent information will be entered on the chain-of-custody record before placement in the shipping container.
    - All shipments will be accompanied by the original chain-of-custody record identifying their contents.

A designated sample custodian at the laboratory will accept custody of the shipped samples from the carrier and enter preliminary information about the package into a package or sample receipt log, including the initials of the person delivering the package and the status of the custody seals on the coolers (i.e., broken versus unbroken). The custodian responsible for sample log in will follow the laboratory's SOP for opening the package, checking the contents, and verifying that the information on the chain-of-custody agrees with samples received. The laboratory will follow its internal chain-of-custody procedures as stated in the laboratory QA Manual.

7.7. Field Log Requirements

During each pre- and post-storm site visit to each monitoring station, the following information will be recorded on a waterproof standardized field form (see Appendix A).

- Name and location of project
- Field personnel
- Sequence of events
- Any changes or deviations from the QAPP or SOPs
- Weather and flow conditions
- Environmental conditions
  - Date, time, location, ID, and description of each sample
  - Identity of QC samples collected
  - Unusual conditions (e.g., oily sheen, odor, color, turbidity, discharges or spills, and land disturbances)
  - Modifications of sampling procedures

7.8. Other Activities

Not applicable.

8. LABORATORY PROCEDURES

8.1. Lab Procedures Table

Table 9 lists the analytical methods, method detection limits, and reporting detection limits that will be used.

Table 9. 6PPD-q Measurement Methods (laboratory).

Laboratory	Sample Matrix	Method Detection Limit	Reporting Detection Limit	Analytical Method
KCEL	Stormwater	0.01 ug/L	0.05 ug/L	KCEL SOP #4077
MEL	Stormwater	0.000368 ug/L	0.001 ug/L	MEL SOP #730136V1.1

8.2. Sample Preparation Method(s)

Sample preparation methods will follow the laboratory SOPs.

Experimental groups HDPE_24 and FLPE_24 for field protocol sampling will be delivered to KCEL in HDPE or FLPE sample bottles. At least 24 hours after the sample collection times listed on these samples, laboratory staff will transfer the contents to amber glass sample containers for storage and analysis with the other samples. The transfer times will be noted by laboratory staff and included in the analytical report.

8.3. Special Method Requirements

Not applicable.

8.4. Laboratories Accredited for Methods

Presently, there are no accredited laboratories for 6PPD-q. Ecology has signed an accreditation-waiver for KCEL for analysis of these samples.

9. QUALITY CONTROL PROCEDURES

9.1. Table of Field and Laboratory Quality Control

Laboratory QC samples for aquatic toxicology analyses and associated control limits are summarized below (Table 10). These QC samples will be analyzed at a frequency of one per analytical batch of 20 or fewer samples. In addition to the discrete QC samples, the recovery of the extracted internal standard/surrogate is monitored in every sample and this recovery must be 20–200 percent.

Table 10. Quality Control Samples, Types, and Frequency.

Parameter	Laboratory Check Standards	Laboratory Method Blanks	Analytical Duplicates RPD	Matrix Spike Percent Recovery	Spike Blank Percent Recovery	Frequency
6PPD-quinone	50-150%	<MDL	40% or ± 2 × RL	50-150	50-150	Once per analytical batch of 20 or fewer samples
6PPD-quinone	50-150%	<1/2 RL	40%	40-160	50-150	Once per analytical batch of 20 or fewer samples

Rinsate blanks will be collected for both lengths of sample tubing prior to collection of field protocol samples and upon completion of field protocol sampling. Tubing will be backflushed with five liters of lab-provided DI water and collected in the field using the peristaltic autosampler.

9.2. Corrective Action Processes

Field activities will be reviewed as soon as practicable following each sampling event, including decontamination method and sample collection locations. If activities are found to be inconsistent with this QAPP, field staff will be asked to review relevant SOPs, and additional sampling may be conducted to replace inadequate data if time allows. For laboratory analyses, the lab may be asked to re-analyze samples that do not meet MQOs if holding times allow.

10. DATA MANAGEMENT PROCEDURES

10.1. Data Recording and Reporting Requirements

Final laboratory data and electronic data deliverables (EDDs) will be stored on Herrera's SharePoint server in the "Data" folder within the project folder (23-08026-000). Field data will be input using field template forms, which will be uploaded upon receipt from the field sampler. Field sheets will be submitted to the project manager within three days business days of the field day. The project manager will save field data in the same folder.

Hand-recorded data will be manually digitized as necessary, with all digitized data undergoing peer review for accuracy.

Based on quality control procedure outcomes (Section 9), values associated with minor quality control problems will be considered estimates and assigned J qualifiers. Values associated with major quality control problems will be rejected and qualified R. Ecology and the analytical lab(s) will be consulted to define major and minor quality control problems. Estimated values may be used for evaluation purposes, whereas rejected values will not be used. Qualifiers and usage are defined in Table 11.

Table 11. Data Qualifier Definitions and Usage Criteria.

Data Qualifier	Definition	Criteria for Use
J	Value is an estimate based on analytical results.	MQOs for field duplicates, laboratory duplicates, matrix spikes, laboratory control samples, holding times, or blanks have not been met.
R	Value is rejected based on analytical results.	Major quality control problems with the analytical results.
U	Value is below the reporting limit.	Based on laboratory method reporting limit.
UJ	Value is below the reporting limit and is an estimate based on analytical results.	Based on laboratory method reporting limit; MQOs for analytical results have not been met.

10.2. Laboratory Data Package Requirements

The laboratory will report the analytical results within 30 days of receipt of the samples. The laboratory will provide sample and quality control data in standardized reports that are suitable for evaluating the project data. These reports will include all raw data including raw quality assurance data, and all quality control results associated with the data. The reports will also include a case narrative summarizing any problems encountered in the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. Laboratory analytical and QA results will be delivered from the laboratory in both electronic and hardcopy form.

10.3. Electronic Transfer Requirements

Laboratories will provide analytical results in electronic data delivery (EDDs) spreadsheets (csv, tsv, or similar) to minimize data entry problems and facilitate data analysis.

10.4. Data Upload Procedures

Not applicable.

10.5. Model Information Management

Not applicable.

11. AUDITS AND REPORTS

The following section describes the procedures used to ensure that this QAPP is implemented correctly, that the data generated is of sufficient quality to meet the project objectives, and that corrective actions, if necessary, are implemented in a timely manner. The procedures include revisions, audits and response actions, corrective actions, and data quality assurance reporting.

If significant changes to this monitoring plan are required prior to the completion of the study, a revised version of the document (with changes tracked) shall be prepared and submitted to the Ecology and Herrera project managers for review. The approved version of the monitoring plan shall remain in effect until the revised version has been approved. Justifications, summaries, and details of expedited changes to the monitoring plan will be documented in the monitoring report.

11.1. Audits

Audits will be conducted for field, laboratory, and data management activities, following the schedule outlined below in Table 12.

Table 12. Quality Assurance Audit Schedule and Response Actions.

Assessment Activity	Approximate Schedule	Responsible Party	Scope	Response Requirements
Field Measurement Audit	Within 7 days of completion of sampling event	Herrera Project Manager	Review of field notes and data	Annotate field notes and notify field staff within 3 days
Laboratory Measurement Audit	Within 7 days of receiving laboratory data reports	Herrera Project Manager	Review analytical and quality control procedures employed at laboratory	Laboratory to respond in writing within 3 days to address corrective actions
Data Entry Audit	Within 7 days of data entry	Herrera Data Manager	Review all data entry values	Correct errors and repeat audit until no errors found

11.2. Responsible Personnel

The responsible personnel for audits are outlined in Table 12 above.

11.3. Frequency and Distribution of Reports

The data collected as part of QAPP execution will be presented in a final report, and the data spreadsheet will be conveyed electronically to the Ecology project manager.

11.4. Responsibility for Reports

The final report will be completed by Herrera.

12. DATA VERIFICATION

Data verification is a systematic process for evaluating performance and compliance of a set of data to ascertain its completeness, correctness, and consistency using the methods and criteria defined in the QAPP.

All data obtained from field and laboratory measurements will be reviewed and verified for conformance to project requirements, and then validated against the data quality objectives which are listed in Section 5. Only those data which are supported by appropriate quality control data and meet the measurement performance specification defined for this project will be considered acceptable and used in the project.

12.1. Field Data Verification, Requirements, and Responsibilities

Field data will be hand-digitized from notes as necessary. Data will then be peer reviewed both for accuracy and reasonableness. Reasonableness will include identifying any data that are noticeably different from nearby samples or previous samples at the same location. Any questionable data points will be relayed to the project manager, who will discuss the questionable data with field staff. A decision will then be made on whether to keep, flag, or discard the data in question. The project manager or a designated staff member will periodically (i.e., at minimum once per quarter) review field data for completeness and legibility.

Roles and responsibilities are as follows:

- The Field Sampler is responsible for ensuring that field data are properly reviewed and verified for integrity.
- The Herrera Data Manager is responsible for entering the data in the project database.
- The Herrera Project Manager is responsible for ensuring that all data are properly reviewed, verified, and submitted in the required format to the project database. The Herrera Project Manager is responsible for validating the data and is responsible for ensuring that all data to be reported meet the objectives of the project and are suitable for reporting.

12.2. Laboratory Data Verification

The project manager or their designee will review and audit laboratory data within 14 business days of receiving the results. This review will be performed to ensure that all data are consistent, correct, and complete, and that all required quality control information has been provided.

The roles and responsibilities are as follows:

- The **Laboratory Manager** is responsible for ensuring that laboratory data are scientifically valid, defensible, of acceptable precision and accuracy, and reviewed for integrity.
- The **Herrera Data Manager** is responsible for entering the data in the project database.
- The **Herrera Project Manager** is responsible for ensuring that all data are properly reviewed, verified, and submitted in the required format to the project database. The Herrera Project Manager is responsible for ensuring that all data to be reported meet the objectives of the project and are suitable for reporting.

12.3. Validation requirements, If Necessary

Formal data validation is defined as: "an analyte-specific and sample-specific process that extends the evaluation of data beyond method, procedural, or contractual compliance (i.e., data verification) to determine the analytical quality of a specific data set" (EPA 2002). This requires a qualified, independent individual to review raw field or instrument records and bench sheets. Data validation is not necessary for this project.

12.4. Model quality assessment

Not applicable.

13. DATA QUALITY (USABILITY) ASSESSMENT

13.1. Process for Determining Project Objectives Were Met

The Herrera project manager or their designee will provide an independent review of the water quality QC data from each sampling event using the MQOs that have been identified in this QAPP. The report will summarize quality control results, identify when data quality objectives were not met, and discuss the resulting limitations (if any) on the use or interpretation of the data. Values associated with minor quality control problems will be considered estimates and assigned *J* qualifiers. Values associated with major quality control problems will be rejected and qualified *R*. Estimated values may be used for evaluation purposes, while rejected values will not be used. All data will be included in the spreadsheet file and the associated study specific qualifiers assigned as part of the usability review.

13.2. Treatment of Non-Detects

We do not anticipate encountering non-detects because the sensitivity of the laboratory method for analyzing 6PPD-q. In the event of non-detects, the treatment will depend on the analysis completed. Methods employed will follow Helsel (2012).

For summary statistics in the presence of non-detects, we will employ the Kaplan-Meier method if multiple detection limits are present or Robust regression on order statistics (ROS). To compute ROS, at a minimum, there must be at least three detected values and a detection frequency greater than 50 percent. In the event of too few detects to reliably calculate summary statistics, frequency of detection will be presented.

For statistical comparisons between groups, we will first replace values below the highest non-detect detection limit with that detection limit. The non-parametric rank-based tests use will treat these as ties. However, if using parametric tests (e.g., ANOVA, t-test, Tukey's test), methods from Helsel (2012) will be employed.

For calculating removals efficiency or loss (see equation below) associated with BMPs or field equipment, we will substitute the detection limit for the non-detect value and flag the resultant value. If C_1 is non-detect and C_2 is detected, we will flag the result as "<", i.e., removal efficiency is at or less than the calculated value. If C_1 is detected and C_2 is non-detect, we will flag the result as ">", i.e., removal efficiency is at or greater than the calculated value. If both C_1 and C_2 are non-detect, we will report a 0 percent removal and flag the result as "J" for estimated.

Note that there are not enough 6PPD-q BMP performance data available from other studies to determine an estimate for an irreducible concentration.

13.3. Data Analysis and Presentation Methods

The reduction (in percent) in 6PPD-q concentration (ΔC) for each sample set (e.g., influent vs. effluent; control vs. Teflon tubing) will be calculated as:

$$\Delta C = 100 * \frac{(C_1 - C_2)}{C_1}$$

Where: C_1 = Influent or control pollutant concentration

C_2 = Effluent or experimental group pollutant concentration

Data compilation, analysis, and graphing will be completed with R. Source code will be made available upon request. Anticipated statistical R packages include NADA2, Survival, and stats. Plotting will be accomplished with ggplot2.

Table 13. Planned Data Deliverables, Analytical Approach, and Presentation.

Deliverable	Analysis	Presentation
Characterization of Stormwater Runoff	Summary statistics	Scatter plot or box plot Summary Table
Evaluation of Removal Efficiency	Paired difference test (Paired t-test, paired permutation test, or Wilcoxon Sum Rank)	Plot of Influent Conc vs. Effluent Conc Boxplot of differences Summary Table of Removal for Each Test Bay
Evaluation of Field Equipment	Paired difference test (Paired t-test, paired permutation test, or Wilcoxon Sum Rank) Control vs. Experiment Group	Plot of Control Conc vs. Experiment Control Conc Boxplot of differences from Control Summary Table of Differences for Each Group
Evaluation of Laboratories	Paired difference test (Paired t-test, paired permutation test, or Wilcoxon Sum Rank)	Plot of Influent Conc vs. Effluent Conc Boxplot of differences Summary Table

13.4. Sampling Design Evaluation

There are limited data for 6PPD-q in the environment, specifically that would be useful for assessing variability of levels within storms and from treatment devices. Because there were insufficient data to characterize environmental variability, we did not complete a power analysis. This is an exploratory study. The findings will be useful in developing future power analyses to detect change related to treatment or sampling procedure.

13.5. Documentation of Assessment

The data useability assessment will be included as part of the final data report for this project.

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APPENDIX A

Field Sheets

HERRERA
Science + Planning + Design

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6PPD-Q CHARACTERIZATION MONITORING FORM

PROJECT: **6PPD-q Characterization and Protocol Dev.** PROJECT NO.: **23-08026-000**

CLIENT: **WA Dept of Ecology**

FIELD PERSONNEL: ______ LOCATION: ______

FLOW CONDITIONS: ______ DATE: ______ TIME: ______

WEATHER: ______

BMP ID:		
	Influent 1	**Effluent 1**
Sample ID:		
Sample Time:		
QA Sample:		
Notes (below):		
	Influent 2	**Effluent 2**
Sample ID:		
Sample Time:		
QA Sample:		
Notes (below):		

Notes:

6PPD-Q FIELD PROTOCOL MONITORING FORM

PROJECT: **6PPD-q Characterization and Protocol Dev.** PROJECT NO.: **23-08026-000**

CLIENT: **WA Dept of Ecology**

FIELD PERSONNEL: ______ LOCATION: ______

FLOW CONDITIONS: ______ DATE: ______ TIME: ______

WEATHER: ______

Experimental Group	Sample ID	Sample Time:	QA Sample
CONT			
HDPE_FT			
HDPE_24			
FLPE_FT			
FLPE_24			
PTFE_TUB			
SILI_TUB			
LAB			

Experimental Group	Sample ID	Sample Time:	QA Sample
CONT			
HDPE_FT			
HDPE_24			
FLPE_FT			
FLPE_24			
PTFE_TUB			
SILI_TUB			
LAB			

Experimental Group	Sample ID	Sample Time:	QA Sample
CONT			
HDPE_FT			
HDPE_24			
FLPE_FT			

FLPE_24			
PTFE_TUB			
SILI_TUB			
LAB			

Experimental Group	**Sample ID**	**Sample Time:**	**QA Sample**
CONT			
HDPE_FT			
HDPE_24			
FLPE_FT			
FLPE_24			
PTFE_TUB			
SILI_TUB			
LAB			

Experimental Group	**Sample ID**	**Sample Time:**	**QA Sample**
CONT			
HDPE_FT			
HDPE_24			
FLPE_FT			
FLPE_24			
PTFE_TUB			
SILI_TUB			
LAB			

Experimental Group	**Sample ID**	**Sample Time:**	**QA Sample**
CONT			
HDPE_FT			
HDPE_24			
FLPE_FT			
FLPE_24			
PTFE_TUB			
SILI_TUB			
LAB			

Experimental Group	Sample ID	Sample Time:	QA Sample
CONT			
HDPE_FT			
HDPE_24			
FLPE_FT			
FLPE_24			
PTFE_TUB			
SILI_TUB			
LAB			

Experimental Group	Sample ID	Sample Time:	QA Sample
CONT			
HDPE_FT			
HDPE_24			
FLPE_FT			
FLPE_24			
PTFE_TUB			
SILI_TUB			
LAB			

Experimental Group	Sample ID	Sample Time:	QA Sample
CONT			
HDPE_FT			
HDPE_24			
FLPE_FT			
FLPE_24			
PTFE_TUB			
SILI_TUB			
LAB			

Experimental Group	Sample ID	Sample Time:	QA Sample
CONT			
HDPE_FT			

HDPE_24			
FLPE_FT			
FLPE_24			
PTFE_TUB			
SILI_TUB			
LAB			

Experimental Group	**Sample ID**	**Sample Time:**	**QA Sample**
CONT			
HDPE_FT			
HDPE_24			
FLPE_FT			
FLPE_24			
PTFE_TUB			
SILI_TUB			
LAB			

Event Notes:

Sample Set 1 Notes:

Sample Set 2 Notes:

Sample Set 3 Notes:

Sample Set 4 Notes:

Sample Set 5 Notes:

Sample Set 6 Notes:

Sample Set 7 Notes:

Sample Set 8 Notes:

Sample Set 9 Notes:

Sample Set 10 Notes:

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APPENDIX B

Chain-of-Custody Form

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Washington State Department of Ecology
Manchester Environmental Laboratory
Chain of Custody

Page ____ of ____

ECY 040-115 (Rev. 07/2019)

Project Name: 6PPD-q Characterization and Protocol Development **MEL Work Order #:** 2305051 **Send Results To:** Morgan Baker

MIC (8 digits): F42133R0 **Program:** Water Quality **Date Results Needed By:** Standard TAT **# of coolers:** ________ **EIM Study ID:** N/A -- do not s

Sampling										General Chemistry																								Micro				Metals (List individual metals and/or request MS/MSD in comments)						Organics (Request MS/MSD and/or dup in comments)															
Date			Time 00:00 – 24:00		Field Station Identification	Sample Number	Matrix Code	Source Code	No. of Containers																																																		
Year	Month	Day	Hour	Min						Alkalinity	Conductivity	pH	Turbidity	Chloride	TOC-440	SSC	TDS	Total Solids	% Solids	TNVSS	TSS	Ash free dry weight	TOC	DOC	BOD5	Oil & Grease	Ammonia	Nitrite/Nitrate	Orthophosphate	Total Phosphorus	TPN	Chlorophyll	Chlorophyll filter	Fecal Coliform MF	Fecal Coliform MPN	E. coli MF	E. coli MPN	Total Metals	Dissolved Metals	Hardness	PP Metals -13 metals	Mercury (Hg)	Hg LL 1631e	BTEX	TPHG	TPHD	VOA	PCB-Aroclors	PCB-Cong HRMS-Cx	Herbicides	PESTMS	Carbamates	PBDE	BNA	PAH	PAH/Phthalates	PAH-SIM	PFAS	6PPD-q
							1 0																																																				x

Chain of Custody Record

Relinquished By	Received By	Year	Month	Day	Hour	Min	Tag # or Seal ID	Seal Condition	Locker #	Cooler Temp °C
Sign name here	ukwila Storage Locker (fill in date and time dropped of									
Tukwila Storage Locker										

Project Officer: Morgan Baker

Phone Number: 360-706-4079

Sampler: ____________

Sampler: ____________

Recorder: ____________

Comments

Login: P81411 **WDOE Stormwater BMP Research** **FSU TC: ____________________**

Project: 421520-200 **LPM: Meghan Elkey**

CHAIN OF CUSTODY

Relinquished by	***Date***	***Time***
Received by	***Date***	***Time***
Sample Numbers		***[All]***

Sample Number	**P81411-1**	**P81411-2**	**P81411-3**
QC Link			
Locator	**I-5 TAPE**	**I-5 TAPE**	**I-5 TAPE**
Short Loc Desc			
Locator Desc	Lake Union Ship Canal TAPE	Lake Union Ship Canal TAPE	Lake Union Ship Canal TAPE
Site	I-5TAPE	I-5TAPE	I-5TAPE
Comments			
Start Date/Time			
End Date/Time			
Time Span			
Sample Depth			
Dept, Matrix, Prod (Cont ID)	4 LG 6PPDQ (43)	4 LG 6PPDQ (43)	4 LG 6PPDQ (43)

APPENDIX C

Ecology Sampling SOP

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Collecting Grab Samples from Stormwater Discharges

Standard Operating Procedure
Version 1.1

July 2018

Publication 18-10-023

Publication and Contact Information

This document is available on the Department of Ecology's website at:
https://fortress.wa.gov/ecy/publications/summarypages/1810023.html

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- Eastern Regional Office, Spokane 509-329-3400

To request ADA accommodation including materials in a format for the visually impaired, call Ecology at 360-407-6600 or visit https://ecology.wa.gov/accessibility. People with impaired hearing may call Washington Relay Service at 711. People with speech disability may call TTY at 877-833-6341.

Table of Contents

Washington State Department of Ecology

Standard Operating Procedure for Collecting Grab Samples from Stormwater Discharges

Version 1.1

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William R. Kammin, Ecology Quality Assurance Officer, Date – 9/16/2009

WQP001

Please note that the Washington State Department of Ecology's Standard Operating Procedures (SOPs) are adapted from published methods, or developed by in-house technical and administrative experts. Published SOPs can be found on Ecology's website http://ecology.wa.gov, search "quality assurance. Their primary purpose is for internal Ecology use, although sampling and administrative SOPs may have a wider utility. Our SOPs do not supplant official published methods. Distribution of these SOPs does not constitute an endorsement of a particular procedure or method.

Any reference to specific equipment, manufacturer, or supplies is for descriptive purposes only and does not constitute an endorsement of a particular product or service by the author or by the Department of Ecology.

Although Ecology follows the SOP in most instances, there may be instances in which Ecology uses an alternative methodology, procedure, or process.

SOP Revision History

Revision Date	Rev number	Summary of changes	Sections	Reviser(s)
6/29/2018	1.1	General updates to dates, references and website throughout. Safety section update.	All	Brandi Lubliner

1.0 Purpose and Scope

1.1 This document delineates the Department of Ecology's Standard Operating Procedure (SOP) for manually obtaining representative grab samples from a variety of stormwater conveyance systems. External users that reference this SOP are expected to describe or reference their own agency or jurisdiction safety protocols in their Quality Assurance Project Plan (QAPP), as this document describes Ecology protocols. This SOP covers the use of intermediate collection devices, but does not describe the operation of unattended automated sampling devices used to collect stormwater samples.

1.2 This SOP provides some example procedures using common methods. This SOP has two main objectives:

1.2.1 Employ standard methods to ensure comparability between data collected by different organizations and groups while using equipment from different manufacturers.

1.2.2 Collect stormwater quality samples at a single point in a stormwater conveyance that will be representative of a site's discharge.

2.0 Applicability

2.1 This SOP describes equipment selection, sampling techniques and site selection that applies to a variety of systems.

2.2 This SOP provides standardized methods for use by a variety of stormwater conveyance systems including pipes, outfalls and open ditch systems. However, in some cases, sampling procedures vary based on the type of equipment used to collect samples.

3.0 Definitions

3.1 **Automated Sampler**: A portable unit that can be programmed to collect discrete sequential samples, time-composite samples or flow-composite samples (WCD, 2007).

3.2 **Grab sample**: A sample collected during a very short time period at a single location (Ecology, 2016).

3.3 **Quality Assurance Project Plan (QAPP)**: A QAPP describes the activities of an environmental data operations project involved with the acquisition of environmental information whether generated from direct measurements activities, collected from other sources, or compiled from computerized databases and information systems (EPA, 2002).

3.4 **Intermediate Sampling Equipment**: Equipment other than the parameter-specific analytical sample bottle used to collect sample water. This equipment is typically used to collect sample water prior to pouring into the appropriate laboratory container and submitting the sample to the laboratory for analysis. Intermediate equipment can include Teflon or plastic water dippers, glass or plastic containers, Van Dorn samplers or Kemmerer Samplers. Note that equipment material must be compatible with the parameters sampled. Certain plastics should not be used when collecting some organic parameters, in particular, oil and grease. Consult your laboratory or refer to bottle type material listed for each parameter in 40 Code of Federal Regulations (CFR) part 136.

4.0 Personnel Qualifications/Responsibilities

4.1 All field staff must be familiar with other standard operating procedures for water quality sampling and/or trained to collect representative environmental samples. This practice will ensure the sampling event is completed efficiently and cross-training on all aspects of sampling will have been completed. Staff must demonstrate a competency for sample collection using appropriate sampling equipment and techniques.

4.2 The field lead directing sample collection must be knowledgeable of all aspects of the project's QAPP and/or project goals and objectives to ensure that credible and useable data are collected. All field staff will be briefed by the Field Lead or Project Manager on the sampling goals and objectives prior to arriving to the site (Ecology, 2016).

5.0 Equipment, Reagents, and Supplies

5.1 A set of sample bottles based on the specific parameters being collected and analyzed (Refer to laboratory and/or most current version of 40 CFR part 136). A good rule of thumb is to bring a few extra sampling bottles during every sampling event.

5.2 Field filtering equipment (if applicable). Consult with your laboratory or check 40 CFR part 136 requirements (e.g., dissolved metals and orthophosphate).

5.3 Field safety equipment including safety vests and/or highly visible clothing, traffic control signs and cones or appropriate field safety forms, and a first aid kit. Refer to Safety Section 9.

5.4 Clean, non-metallic ice chest with ice and plastic barrier. (An ice barrier is a layer of plastic between the sample containers and the ice within an ice chest to prevent potential contamination from ice melt.)

5.5 Personal protective equipment including hardhats, goggles, earplugs, waders, water boots, and powder free gloves.

5.6 Decontamination equipment including distilled water, de-ionized water, wash and rinse spray bottles, appropriate detergents or pesticide grade acetone and/or nitric acid (10% solution) if applicable.

5.7 Writing instruments, driving directions, clip board, and *Rite-in Rain*™ field sheets or notebook.

5.8 Plastic tub/disposal container to collect excess rinsate from your decontamination procedure.

5.9 Water quality meters (pH, conductivity, temperature).

5.10 Miscellaneous hardware: flashlights and head lamps, shovel and brush removal tools, Allen wrench, manhole hook and sledge hammer, measuring tape, extra batteries for field instruments, dry chemical hand warmer heat packs, hand sanitizer, rope, duct tape, ty-raps (and diagonal cutter), survey tape, fluorescent spray paint.

5.11 Intermediate sampling equipment. If using Van Dorn or Kemmerer samplers, refer to Ecology's Standard Operating Procedure for Manually Obtaining Surface Water Samples, V1.3, (July 2016).

6.0 Summary of Procedure

6.1 Select a Representative Sampling Location

6.1.2 Determine the most representative site to safely collect samples and achieve project goals and objectives. The sampling location will be placed at the most downstream location that incorporates all of the targeted drainage area. Drainage areas can include urban, rural, roadways, industrial facilities and/or commercial facilities, mixed uses, or areas conveyed to or from best management practices (BMPs).

6.1.3 Prior to sample collection, review all maps, engineering drawings and reports, hydraulic and hydrology reports, and/or site logs, schedules, to determine an appropriate sampling location to understand when and where onsite activities are taking place for safe site accessibility.

6.1.4 Sampling sites should be free-flowing and not affected by backwater and/or tidal conditions. Proper selection of the sampling location assures the collection of representative samples.

6.1.5 The grab sample location must be located in an area where there is adequate mixing to assure that the samples represent water from the targeted drainage area. Sampling mid-stream in the pipe/channel is a good way to ensure collection of a representative sample If low flow conditions exist, it may not be possible to collect mid-stream in the pipe/channel. For low flow conditions, collect the entire sample stream.

6.1.6 Stormwater grab samples must be collected before the stormwater enters a receiving water body.

6.1.7 Selected sites must have ease of access for vehicles and personnel for safe sample collection activities under the full range of weather conditions that may be encountered.

6.1.8 Additional guidance for collecting grab samples from industrial and construction can be found in references 10.6 and 10.7 in the References Section of this document.

6.1.9 Once sampling locations are identified, the area will be labeled using flagging or labeling on a map with proper direction to the site.

6.2 Pre-sampling Site Visit

6.2.1 The sampling site will be inspected for identification of illegal discharges or illicit connections. The sampling location will be visited during wet and dry weather. The inspection will include an evaluation of the following:

6.2.1.1 Presence of debris

6.2.1.2 Signs of staining

6.2.1.3 Odors

6.2.1.4 Water/discharge discoloration

6.2.1.5 Unusual flows

6.2.1.6 Excessive sediment/solids deposits

6.2.1.7 Unexpected inflow pipes of unknown origin

6.2.2 A wet weather visit can provide information such as discharge flow conditions. The dry weather visit can provide information about dry weather flows, i.e., non stormwater flows. A list of criteria specific to the program objectives should be developed prior to visiting the site. A site visit log form can be developed from this list and filled out during each visit.

6.2.3 Inspect the runoff stream for adequate depth for sampling.

6.2.4 Note the following information in field note books or field data sheets:

6.2.4.1 Contributing land use drainage area

6.2.4.2 Presence/absence of illicit discharges and/or connections

6.2.4.3 All possible site hazards

6.2.4.4 Equipment needed in order to access sites (for examples tools for mechanical opening, waders or reflector vests) and equipment needed to collect the sample.

6.3 Procedure Preparation

6.3.1 Obtain proper sample bottles from the laboratory and arrange for sample analysis.

6.3.2 Gather appropriate equipment (see Equipment List).

6.4 Site Set-up Safety Procedures

6.4.1 Set up safety markers around site such as cones and lights.

6.4.2 Establish access to sampling location, such as open manhole, vault, or ditch.

6.4.3 If sampling location is in a ditch or open conveyance and wading is required, determine a safe point of entry. If deemed safe, enter just downstream of sample site.

6.4.4 Wade in a manner to avoid disturbing the sediment/solids and causing water turbidity.

6.4.5 Sampling personnel will wear chemical-resistant gloves whenever coming into contact with potentially hazardous water or chemical preservatives (NPDES SOP, 2008).

6.5 Collecting Grab Samples from BMPs

6.5.1 In cases where water directly discharges from a drainage area through a stormwater treatment BMP (detention pond, swale), sampling will be collected from discrete location(s) (inlet, outlet or both) depending on the QAPP or project goals and objectives.

6.5.2 Determine total number of inlets/outlets. If more than one inlet/outlet exists, several grab samples may be collected for better representation in order to characterize multiple inlets/outlets.

6.5.3 Ensure BMP sampling location reflects the intended sample accurately. For example, note if pre-treatment exists, and if the sampling location for inflow occurs above or below the pre-treatment. In most cases there should be no pre-treatment stormwater prior to the BMP.

6.5.4 Refer to procedures below when sampling from BMPs using sample bottles or when using intermediate equipment.

6.6 Grab Sample Collection Procedures for Direct Sampling of Stormwater without the Use of Intermediate Equipment

6.6.1. For parameter sequencing prior to filling containers, refer to 6.9 below

6.6.2 Access sampling location

6.6.3 Remove stopper/lid from sample bottle just before sampling. Be careful not to contaminate the cap, neck, or the inside of the bottle with your fingers, wind-blown particles, or dripping water from your clothes, body, or overhanging structures (Ecology, 2016).

6.6.4 If preservative is ***not*** present in the container, face container upstream and proceed as follows:

6.6.4.1 Hold the container near its base, reach out in front as far as possible, and plunge the sample bottle (mouth down) below the surface to about elbow depth if the sediment/solids will not be disturbed (Ecology, 2016).

6.6.4.2 Fill the bottle to the appropriate level depending on the analyte to be tested (Ecology, 2016).

6.6.4.3 Pour out a small volume if needed to create a headspace for mixing in the lab. Do not create a headspace for some analytes like volatile organics (Ecology, 2016).

6.6.4.4 Securely replace the lid of the container. Invert it several times to evenly mix preservative with the sample.

6.6.4.5 Rinse any large amount of dirt or debris from the outside of the container.

6.6.4.6 Refer to section 6.8 for bottle labeling and place directly on ice in appropriate storage

6.6.4.7 Put a note in the field notebook if you suspect that sand or other heterogeneous materials were not adequately represented in the sample.

6.6.5 If preservative ***is*** present in the container and you can reach the water with your hand, use the following procedure:

6.6.5.1 This procedure does not work well in forceful jets of water from drains and outfalls (Ecology, 2016).

6.6.5.2 Hold the container upright and place the lid over the mouth so that only a small area forms an opening (Ecology, 2016).

6.6.5.3 Immerse the bottle 15 cm (6 in) while holding the cap in position with your fingers as far away from the opening as possible (Ecology, 2016).

6.6.5.4 Carefully observe the rate the container is filling and remove it from the water before the headspace area is reached or overfilling occurs (Ecology, 2016).

6.6.5.5 Follow steps 6.6.4.4 – 6.6.4.7 above.

6.7 Grab Sample Collection Procedures Using Intermediate Equipment

6.7.1 For parameter sequencing prior to filling containers, refer to 6.9 below.

6.7.2 Access the sampling site.

6.7.3 Use clean, decontaminated intermediate equipment and rinse equipment with site water prior to sampling (Ecology, 2016).

6.7.4 If an *extension pole* is used with bottles securely attached, remove the lid from the sample bottle being careful not to contaminate the container and follow the procedures in Section 6.6 above (Ecology, 2016).

6.7.5 If any other type of intermediate equipment is used, reach the equipment to the mid-stream column of the discharge stream and collect a water sample.

6.7.6 Bring the sample to a clean, decontaminated area, remove the lid from each container, being careful not to contaminate the cap, neck, or the inside of the bottle with your fingers, wind-blown particles, or dripping water from your clothes, body, or overhanging structures (Ecology, 2016).

6.7.7 Gently mix the water in the intermediate container by inverting (swirling only if there is no cap) before pouring it into the sample containers and/or field filter (if applicable). Field filter any samples prior to pouring water into sample bottles (Ecology, 2016).

6.7.8 For low flow conditions, submerge the equipment into the entire sampling stream and fill bottles. You may have to repeat filling if the intermediate equipment is not able to contain all the volume needed to fill all the sample bottles. Repeat volume collection until bottles are filled.

6.7.9 Fill the sample bottles to the appropriate level depending on the analyte to be tested (Ecology, 2016).

6.7.10 Pour out a small volume if needed to create a headspace for mixing in the lab. Do not create a headspace for some analytes like volatile organics (Ecology, 2016).

6.7.11 Follow steps 6.6.4.4 – 6.6.4.7.

6.8 Labeling Sample Bottles

6.8.1 Bottles should be labeled prior to filling using permanent, waterproof marker on preprinted, waterproof labels. Label all sample bottles clearly with the following information:

6.8.2 Station number

6.8.3 Date and Time

6.8.4 Sample designation (established by the laboratory according to the parameters to be analyzed)

6.8.5 Preservatives added, if appropriate

6.8.6 Sampler's initials

6.9 Sample Processing

6.9.1 If the sample water is highly turbid, the laboratory may need to modify its analytical method for fecal coliform. Consult with the laboratory as soon as possible so they can prepare for adjustments (Ecology, 2016).

6.9.2 For details on parameter-specific bottle types, preservatives and field filtering requirements use the most recent edition of Code Federal Regulations Title 40, part 136 (40 CFR part 136) and/or obtain accurate information from your laboratory.

6.9.2.1 For ***organic*** compounds process raw samples first, followed by filtered samples. Do not field rinse bottles and chill immediately. For ***inorganic*** compounds process raw samples first, followed by filtered samples. Field rinse each bottle with same water that will fill the sample bottle (USGS, Chapter A5, 2002).

6.9.2.2 Organic constituents should be processed using the following priority order: microbiology, organic compounds (whole water or unfiltered) samples first, followed by filtered samples (**do not field rinse bottles),** volatile organic compounds, pesticides, herbicides, polychlorinated biphenyls (PCBs) and other agricultural and industrial organic compounds, total organic carbon (TOC), dissolved organic carbon (DOC), and suspended organic carbon (SOC) (USGS, Chapter A5, 2002).

6.9.2.3 Inorganic constituents should be processed using the following priority order: metals (whole water or unfiltered) samples first, followed by filtered samples, separate-treatment constituents (such as mercury, arsenic, selenium) and major cations, trace metals, mercury, major anions, alkalinity then nutrients (USGS, Chapter A5, 2002).

6.10 Sample Transport and Reporting/ Login Procedures

6.10.1 Complete Chain of Custody procedures.

6.10.2 For immediate delivery to the laboratory after sampling:

6.10.2.1 Pack samples in regular cubed or crushed ice and deliver to the laboratory (with chain of custody).

6.10.3 For next day or after weekend delivery to the laboratory:

6.10.3.1 Keep the samples at a temperature ranging between 4º C and 6º C (Ecology, 2016).

6.10.3 For samples shipped via air or ground freight service:

6.10.3.1 Pack samples using blue ice packs, loose ice in freezer bags or dry ice (check with airline prior to using dry ice for any restrictions).

6.10.3.2 Cool between 4º C and 6º C and store in a dark cooler.

6.10.3.3 Place the Chain of Custody (once completed) into a plastic bag and place inside the cooler.

6.10.3.4 Tape cooler shut and ship to appropriate laboratory address (Ecology, 2016).

6.11 Decontamination

6.11.1 Intermediate equipment (or any other re-usable equipment used for sampling) will be cleaned prior to use and after use using non-phosphorus detergents and rinsed with laboratory grade de-ionized water.

6.11.2 Do not decontaminate sample bottles prior to sample collection. If the sampled parameters require specialized cleaning of bottles, consult with your laboratory.

7.0 Records Management

7.1 *Field sheet data for each sample should include*:

7.1.1 Monitoring station location

7.1.2 Personnel - Initials of Sampling Personnel

7.1.3 Time of sample collection

7.1.4 Sample Method (i.e. intermediate equipment used or individual sample containers)

7.1.5 Field observations that could affect the quality of the samples

8.0 Quality Control and Quality Assurance Section

8.1 Quality Assurance/Quality Control (QA/QC) should be addressed on a project-by-project basis and defined in the QAPP or in project goals and objectives.

8.2 Check the bottle type and materials in the equipment used for sampling to ensure compatibility with every monitored parameter. Also, decontamination detergents and procedures must also be compatible with equipment used and parameters tested.

8.3 Keep sample containers capped during storage at the laboratory and throughout the entire sampling run, except at the exact sampling period.

9.0 Safety

9.1 There are many hazards associated with sampling stormwater. Some of these hazards include fast moving water, deep water, and steep slopes to sampling sites and hostile dogs or people. Use extreme caution when exiting vehicles, walking along busy roads and approaching your sampling site.

9.2 Safety is top priority for field staff and supervisors. Sample sites may be located on or near roads and bridges. Roadside hazards, weather conditions, accidents, and construction should be evaluated before departure (especially in winter). If the hazard is a permanent condition, relocation of the station may be necessary. Review periodically to assist with these safety determinations.

9.3 Develop a site specific safety plan based on the Environmental Assessment Program Safety Manual (Ecology, 2016) and the Chemical Hygiene Plan (Ecology, 2018b).

10.0 References

10.1 U.S. Geological Survey, Techniques of Water-Resources Investigations, Book 9 Handbooks for Water-Resources Investigations, National Field Manuals for the Collection of Water Quality Data, Chapter A3, *Cleaning of Equipment for Water Sampling*, 2004, Chapter A4, *Collection of Water Samples*, 2006, and Chapter A5, *Processing of Water Samples*, 2002.

10.2 Washington Conservation District, Water Monitoring Program, *Standard Operating Procedure (SOP) No. 1: Automated Water Sampling*, Version 2, July 17, 2007.

10.3 Washington State Department of Ecology, Environmental Assessment Program, *Standard Operating Procedure for Manually Obtaining Surface Water Samples*, October 2006. Version 1.3 Recertified July, 2016

10.4 Washington State Department of Ecology, *How to do Stormwater Monitoring: A guide for construction sites, Publication # 06-10-020,* November 2007.

10.5 Environmental Protection Agency Code of Federal Regulations, Title 40, Protection of Environment, July 1, 2008.

10.6 Florida Department of Protection, *FS 2100 Surface Water Sampling,* DEP-SOP-001/01, March 31, 2008.

10.7 Washington State Department of Ecology Publication #02-10-071, *How To Do Stormwater Monitoring, A Guide for Industrial Facilities*, December 2002, revised 2009.

10.8 City of Tacoma, Pierce County, Clark County and Snohomish County, NPDES Collaborative Stormwater Monitoring Program, SOP NPDES DS 2000 – *Standard Operating Procedures for the Grab Sampling of Surface Storm Water*, May 27, 2008.

10.9 U.S. Department of Transportation, Federal Highway Administration, *Guidance Manual for Monitoring Highway Runoff Water Quality,* Publication No. FHWA-EP-01-022, June 2001.

10.10 Ecology, 2016. Environmental Assessment Program Safety Manual. Olympia, WA. 168 pp.

10.11 Ecology, 2018. Chemical hygiene plan and hazardous material handling plan. Olympia, WA.