Testing Removal of 6PPD-Q and Coho Salmon Lethality by High Performance Bioretention Media Blends: Final Quality Assurance Project Plan

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King County

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Quality Assurance Project Plan

Testing Removal of 6PPD-Q and Coho Salmon Lethality by High Performance Bioretention Media Blends

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1.0 INTRODUCTION

This quality assurance project plan (QAPP) describes a study to determine the effectiveness of three high performance bioretention soil media (HPBSM) configurations in reducing or eliminating acute lethality of untreated stormwater to coho (*Oncorhynchus kisutch*) salmon (urban runoff mortality syndrome, or URMS) and its causes. The project is partially funded by the State of Washington Department of Ecology (Ecology). Both King County's technical objectives and Ecology's related project requirements are reflected in this QAPP.

1.1 Background Information

Bioretention systems are used to treat polluted stormwater and control flashy urban runoff. Bioretention is considered a type of Green Stormwater Infrastructure and is included in the suite of Low-Impact Development (LID) techniques for stormwater treatment. The state of Washington requires Phase I and Phase II jurisdictions to use LID practices as their first option, where possible, for treating and controlling stormwater runoff under the state's municipal stormwater NPDES permit. Bioretention systems can be configured in various ways, depending on site-specific treatment goals and priorities. Ecology specifies acceptable bioretention configurations, including the components and installation of bioretention soil mix (BSM).

1.1.1 Summary of Previous Studies

Untreated stormwater from some locations in King County contains 2-anilino-5-(4-methylpentan-2-ylamino)cyclohexa-2,5-diene-1,4-dione, a.k.a. 6PPD-quinone (6PPD-Q), a toxic chemical that causes URMS in coho and is also toxic to several other aquatic species (Tian et al. 2021, 2022; Brinkmann et al. 2022; Hiki et al. 2021). Bench-scale lab studies have shown that bioretention systems using a BSM containing compost can eliminate coho toxicity. A high-compost BSM consisting of 60% sand and 40% compost by volume (60/40 BSM) is the current default approved treatment medium for bioretention systems in western Washington. The 60/40 BSM is reliably effective at removing some contaminants from stormwater, including total suspended solids, and hydrocarbons. However, this default BSM has been shown to export nitrogen and phosphorus in the treated effluent. Findings on treatment of metals are mixed. To protect surface waters from nutrient inputs, Ecology prohibits use of bioretention systems containing the default 60/40 BSM in certain project locations: those within one-quarter mile of phosphorus-sensitive receiving waters if underlying soils fail to meet suitability criteria or if an underdrain would route effluent to phosphorus-sensitive receiving waters.

An ideal bioretention system would effectively treat influent water for a range of contaminants and protect aquatic organisms from toxic compounds carried by stormwater while also preventing nutrient and metal export to receiving waters. A system meeting these criteria would be suitable for installation in many more project sites, resulting in greater stormwater treatment capacity in our rapidly developing region. This would also

provide a new and urgently needed tool for addressing 6PPD-Q in stormwater and prevent it from contaminating surface water habitats for valued fish resources.

Studies of several high-performance HPBSM blends have shown that these media options can effectively reduce several different contaminant concentrations in stormwater and eliminate nutrient and copper export (Herrera 2020, 2022). Initial toxicity studies using the water flea (or zooplankton *Ceriodaphnia dubia*) and zebrafish (*Danio rerio*) suggested that HPBSM blends tested may protect aquatic life from acute toxicity of stormwater runoff. One of the blends tested, using a primary layer of volcanic sand, coconut coir, and high carbon wood ash (biochar), performed well for metals reduction (i.e., met Ecology's enhanced treatment objectives) but did not meet objectives for total phosphorus (TP) reduction. Another blend, using the same primary layer and a polishing layer underneath (including activated alumina and iron to adsorb nutrients and copper), even with 2 inches of compost mulch on top, met all of Ecology's criteria for basic, enhanced, and phosphorus treatment. The polishing layer successfully removed nutrients shown to leach from compost in previous studies (Herrera 2016). This 3-layer HPBSM with the compost mulch also supported robust plant growth.

Table 1. Components and Application of High Performance Bioretention Media

	Basic Treatment	Enhanced Treatment	Phosphorus Treatment	Expanded Plant Palette and Robust Plant Growth
Primary layer	X	X		
Primary plus polishing layer	X	X	X	
Primary plus polishing layer plus compost mulch[a]	X	X	X	X

Note: The components of the bioretention media in Table 1 are as follows: Primary layer: 70 percent sand/20 percent coir/10 percent high carbon wood ash (biochar); Polishing layer: 90 percent sand/7.5 percent activated alumina/2.5 percent iron aggregate; Compost mulch: coarse compost meeting Ecology's compost specifications for bioretention.

In 2021, Ecology approved the use of all three blends, and expects to include them in the next updated stormwater manual. HPBSM with a polishing layer either underneath or in a treatment train can now be used within one-quarter mile of phosphorus-sensitive receiving waters. Whether any or all of the HPBSM systems are also effective in controlling URMS is a critical data gap.

1.1.2 Problem Statement

The direct link between URMS and 6PPD-Q specifically as a stormwater constituent is a relatively new finding and much about this chemical is still unknown. 6PPD-Q is an oxidation biproduct of another chemical (the tire additive N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine, or 6PPD), and both chemicals are unstable in the environment, complicating research on treatment. The initial toxicity studies with the Ecology-approved HPBSM evaluated survival and reproductive toxicity to water fleas and zebrafish and neurotoxicity in zebrafish. However, the study did not test for coho URMS

symptoms, or characterize water samples for 6PPD-Q. Toxicity studies using the HPBSM have not yet been done on coho, a salmonid shown to be very sensitive to 6PPD-Q.

1.2 Scope and Purpose

This QAPP outlines the steps the Project Team intends to take to answer the research questions described below and provide recommendations to Ecology and the King County Stormwater Services Section (SWS). It includes data quality objectives (DQOs), method quality objectives (MQOs), study design, experimental procedures, and plans for quality control and data management.

1.3 Study Area and Surroundings

The project described by this QAPP is an experiment to be performed in laboratories. The stormwater to be tested will be collected from a single location, as described in Section 2. The location provides access to stormwater that drains directly from Interstate Highway 5 (I-5) and adjacent densely developed urban residential land.

2.0 PROJECT DESCRIPTION

The present study builds on prior work to explore whether HPBSM blends can protect coho salmon from URMS, and assess the potential effectiveness of each approved bioretention media at the bench scale. .

2.1 Project Goals

King County seeksinformation on the relative effectiveness of the three Ecology-approved configurations of the HPBSM (HPBSMx) in reducing concentrations of 6PPD-Q in stormwater (Ecology 2021), and thereby reducing risk of URMS in freshwaters within King County.

The **primary goal** of this bench-scale study is to determine if and measure the extent to which 60/40 BSM and the three Ecology-approved HPBSM configurations reduce the concentration of 6PPD-Q in stormwater to below levels toxic to coho, eliminate coho toxicity, or both; and if any of the Ecology-approved HPBSMx performs better or worse at this function than 60/40 BSM. This project includes both chemical analysis of treated and untreated stormwater for 6PPD-Q and direct toxicity tests with juvenile coho salmon.

In addition, a **secondary goal** of the study is to identify and measure stormwater constituents and conditions (e.g., pH, dissolved oxygen; see Section 2.2.1), that may be dynamic in stormwater and may also be affected by these approved bioretention media types. We will evaluate how common water quality characteristics change during each cycle in the experiment, and the degree to which they change due to passing through the BSM columns.

Addressing the **secondary goal** includes measuring dissolved organic carbon (DOC)), total suspended solids (TSS) in untreated and treated stormwater effluents, to evaluate whether these parameters affect the outcome of toxicity tests, e.g., through binding 6PPD-Q.

Results will provide insights into how stormwater treatment acts to affect 6PPD-Q concentrations and to reduce toxicity.

2.2 Study Questions and Design

The study described in this QAPP consists of bench-scale soil column tests of three HPBSM types and the 60/40 BSM for effectiveness in reducing concentrations of 6PPD-Q and/or coho toxicity from field-collected stormwater. The following specific bioretention media types approved for use in LID by Ecology, and to be represented in this study are (percentages are by volume):

1. **Type 1**: 18-inch HPBSM primary layer consisting of: 70% sand, 20% coir, 10% biochar, plus a 12-inch drainage layer of sand.

2. **Type 2**: 18-inch HPBSM primary layer plus 12-inch polishing layer. The polishing layer consists of 90% sand, 7.5% activated alumina, and 2.5% iron aggregate.
3. **Type 3**: Type 2 HPBSM, plus 2-inch compost surface layer meeting Ecology's bioretention compost specifications.
4. **Default 60/40 BSM**: 60% sand/40% compost.

Of the four stormwater treatment types, three will be tested for effectiveness in reducing or eliminating acute lethality to juvenile coho in controlled laboratory toxicity tests (Type 1, Type 3 and 60/40 BSM).

All BSM will be tested using stormwater collected from a single location (Figure 1) and consisting of runoff directly from I-5 during three separate storms. At this location, sampling can be safely performed using existing sampling infrastructure, including two vaults that receive a mix of right of way and paved runoff from I-5 above.

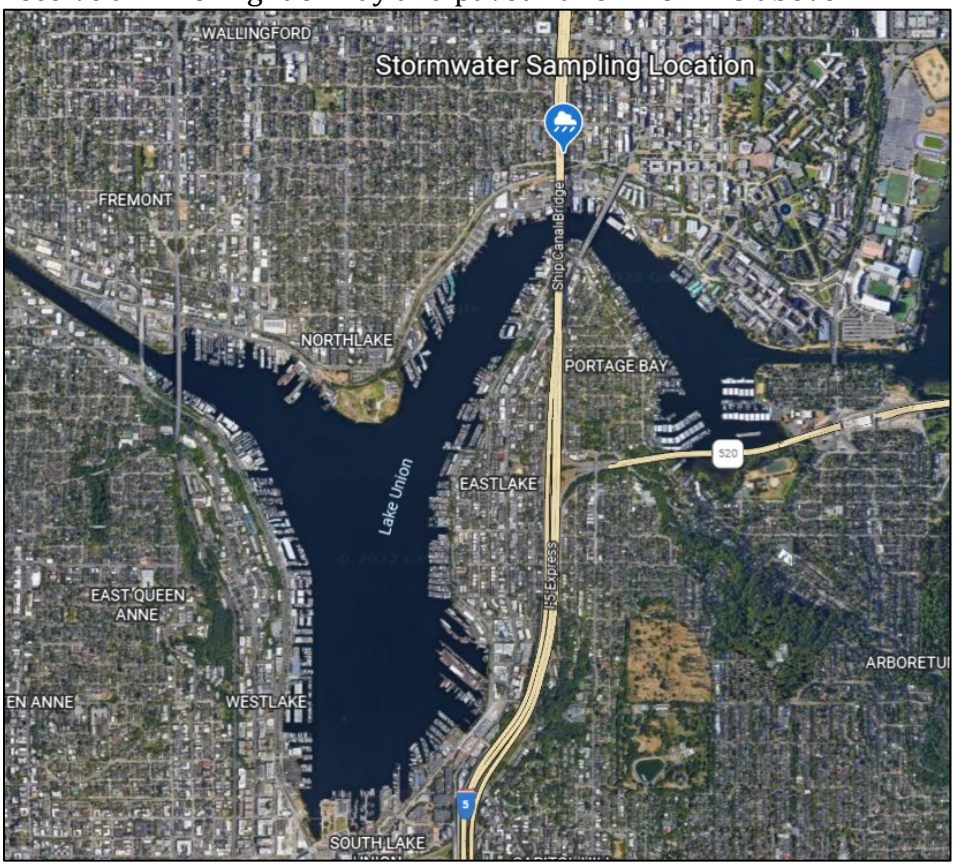

Figure 1. Stormwater Sampling Location

The site receives runoff from a 12.8-hectare (31.6 acres) drainage area including 9.2 hectares (22.7 acres) of pavement and 3.6 hectares (8.9 acres) of roadside landscaping. It is not subject to treatment upstream of the sample collection port.

2.2.1 Study Questions

The Project Team used EPA's 7-step DQO planning process. Our DQOs articulate the problems to be addressed, the goals of the study, study questions and specifications for the study performance to address the study questions. We developed two interrelated DQOs:

- DQO-1. 6PPD-Q removal or reduction effectiveness
- DQO-2. Stormwater toxicity removal or reduction effectiveness

Full DQO summaries with complete statements of each of the 7 steps are presented in Appendix A. Within the context of our DQOs, the study questions are listed below.

DQO-1. 6PPD-Q removal or reduction effectiveness

1. Is the concentration of 6PPD-Q in untreated stormwater influent ≥ the concentration of 6PPD-Q in treated effluent for 60/40 BSM and HPBSMx?
2. Which BSM or HPBSMx generates the greatest reduction in the concentration of 6PPD-Q?
3. Does treatment of stormwater with BSM or HPBSMx generate effluent with the concentration of 6PPD-Q ≤ 0.060 µg/L[1]? Does treatment of stormwater with BSM or HPBSMx generate effluent with the concentration of 6PPD-Q < the method detection limit (MDL)?
4. Is the overall performance of the HPBSMx in removing 6PPD-Q as good or better than that of 60/40 BSM?

DQO-2. Stormwater toxicity removal or reduction effectiveness

1. Is treated stormwater effluent from 60/40 BSM and HPBSMx Types 1 and 3 acutely toxic to coho?
2. Is untreated stormwater influent more or less acutely toxic to coho than treated stormwater effluents?
3. What are the concentrations of 6PPD-Q measured in toxic stormwater and in non-toxic stormwater? (see DQO-1)
4. Do certain constituents of treated stormwater effluent (DOC and TSS) covary with toxicity to coho? These constituents may affect toxicity by binding to 6PPD-Q.

To date, published studies that measure both 6PPD-Q concentration and toxicity to coho in field-collected stormwater are rare. Among the findings of Tian et al. (2021) was that the toxicity of 6PPD-Q to coho (as the LC_{50} value) differed by a factor of 3 in tire leachate samples diluted with two separate stormwater samples. In contrast, toxicity results for 6PPD-Q in two leachate solutions diluted with laboratory water were very consistent (Tian et al. 2021). Moreover, the toxicity of 6PPD-Q in stormwater in that experiment was both

[1] The LC_{50} for coho exposed to 6PPD-Q in the laboratory is 0.095 µg/L (Tian et al. 2022). Coho is the most sensitive aquatic species to 6PPD-Q toxicity identified to date. To establish a less toxic concentration, we estimated the LC_{20} at 0.060 µg/L from results presented by Tian et al. (2022). We will use the estimated LC_{20} concentration to address this study question.

higher and lower than in the controlled leachate solutions. This result suggests that characteristics of the stormwater itself that were not measured in Tian et al.'s (2021) experiments affected toxicity of the 6PPD-Q. Stormwaters are complex mixtures of many chemicals (Ecology 2015), and although the reasons for differences in toxicity between Tian et al.'s (2021) two stormwater-diluted 6PPD-Q mixtures are unknown, variation in basic water quality parameters that are readily measured may provide useful insights.

Therefore, this study will measure commonly measured water characteristics in each stormwater sample at the time of sampling, and throughout the experiment. These include pH, temperature, oxidation-reduction potential (ORP), specific conductance, and dissolved oxygen (DO) content. These will be measured in stormwater at various time points of each storm cycle, including before and after bioretention treatment as well as when toxicity tests are conducted. In addition, water used in toxicity tests will be measured for TSS and DOC. Our data analysis will explore a general study question about the variability in these stormwater physical and chemical conditions between storms and at points throughout the treatment process. We anticipate this information will help us to better understand how bioretention treatment functions with respect to these water quality characteristics.

These study questions govern the process for performing the project, presented in the next section. By addressing each question, this study will develop evidence regarding the potential effectiveness of each HPBSMx to address URMS, and the effectiveness of each relative to that of 60/40 BSM.

2.2.2 Experimental Design

This section presents the experimental design, including a summary of the approach and phases of the study, description of the column array, water delivery, and water sampling. These bullets summarize the approach; numbers of each sample type at each point are in Table 2.

The experimental design can be summarized as follows:

- **Number of storms**: Stormwater will be collected during three separate storm events in 2023. Stormwater runoff will be directed into a set of 20-L fluorinated high density polyethylene carboys at I-5 Ship Canal and transported to the Bioretention Laboratory, where it will be composited.
- **Represented water year**: A series of stormwater dosing with sampling will be interspersed with dosing without sampling sufficient in combination to represent approximately 81% of a Seattle water year.
- **Number of bioretention media types**: Stormwater samples from each storm will be filtered through four types of bioretention soil media: 60/40 BSM and Types 1, 2 and 3 HPBSM (defined above).
- **Replicationeach media type**: For dosing events with sampling, each bioretention media type will be tested in triplicate per storm, for a total of 12 effluent samples per storm.

- **6PPD-Q concentrations, untreated stormwater grab:** For dosing events with sampling, a grab sample of untreated stormwater will be sent to King County Environmental Laboratory (KCEL) for immediate analysis of 6PPD-Q (N=1 per storm). A split of this grab sample will travel with the stormwater sample for testing and be analyzed for 6PPD-Q at the time toxicity test waters undergo this analysis.
- **6PPD-Q concentration and toxicity in samples of the untreated influent and bioretention media-treated effluents:** Following compositing of the untreated stormwater sample:
    - The untreated influent will be sampled during application of the stormwater sample to the media columns. The untreated influent will be analyzed for 6PPD-Q, TSS, DOC and water quality characteristics (N=3 per storm).
    - In addition, approximately 20 L of the untreated influent composite will be sampled and preserved at ≤4°C in the dark for later toxicity testing (N=1 per storm).
    - Treated stormwater effluents will be collected from each bioretention media column, and will be subsampled into:
        - 0.25 L for analysis of 6PPD-Q (N=12 effluent samples per storm)
        - 0.3 to 0.5 L for measurement of water quality characteristics (N= 12 effluent measurements per storm)
        - 1 L for analysis of TSS (N=12 samples per storm)
        - Approximately 6.6 L from each column replicate within a media type will be composited into one effluent sample of approximately 20 L. These will be used in acute toxicity testing with juvenile coho salmon (N= 4 composited treatment effluents per storm).
            - Only the untreated influent and effluents from 60/40 BSM, HPBSM Type 1 and HPBSM Type 3 will be included in toxicity testing.
                - Composited effluent from Type 2 HPBSM will not be tested for direct toxicity but will be tested for 6PPD-Q.
        - At the time of toxicity testing, aliquots of each effluent composite to be used in toxicity tests will be sampled and tested for 6PPD-Q, TSS, DOC and water quality characteristics (N= 4 per storm for treated effluents) for use in interpreting toxicity test results.
- **Potential covariates with 6PPD-Q concentration and toxicity**: The following additional water quality characteristics will be collected (summarized in Table 2):
    - **Water quality characteristics**. Characteristics of stormwater that may vary between storms and change due to bioretention treatment: pH, temperature (°C), dissolved oxygen (DO mg/L), oxidation reduction potential (ORP, mV), and specific conductance (mS/cm)
    - **Toxicity covariates.** Characteristics that may affect toxicity of 6PPD-Q include DOC (mg/L) and TSS (mg/L)

- **Toxicity test parameters.** standard test parameters for acute fish toxicity tests include DO, pH, temperature, conductivity, ammonia (unionized calculation), alkalinity and hardness in toxicity test chambers, to be measured according to the EPA Test Method 2019.0.

Table 2 is a summary of the samples and measurements to be collected and the time points during each storm event that each is collected.

Time point definitions shown in Table 2, by location, are:

- Stormwater sampling location in Seattle
  - T_0 – time that stormwater is collected
- Bioretention Laboratory
  - T_1 – time that stormwater samples are composited and homogenized
  - T_2 – time that stormwater treatment is complete and effluent sampling is underway
- King County Environmental Laboratory
  - T_3 – time that all samples arrive at KCEL
  - T_4 – time that toxicity tests are conducted.

In addition to the basic experimental design described above, the project includes quality assurance/quality control (QA/QC) steps, as described further below.

Table 2. Number of Measurements per Storm Event

Parameter	Time Point	Flush Water (Metals, TSS, DOC)	6PPDQ	Coho Toxicity	Water Quality (pH, Temp., DO, ORP, SC)	Toxicity Mitigation Factors (DOC, TSS)
Experimental process point						
6PPD-Q sorption loss to equipment	Pre-trial					
Spiked rinse, partial column equipment (pumps, tubes, etc.) (spiked D.I. water)		--	2	--	--	--
Prior to preparing BSM/HPBSMx columns						
Rinsate blank, subset of bioretention media column array (D.I. water)		--	1	--	--	--
Rinsate blank, bioretention media column used in loss-to-equipment test (D.I. water)		--	1	--	--	--
Rinsate blank, sampling vessels (D.I. water)		--	1	--	--	--
Flush rinse, following column prep, prior to testing						
Flush water tests, effluent composites from treatment types ready for testing (D.I. water)		8	4	1 FHM	0	0
Untreated (Bellingham) stormwater for dosing-without-sampling						
Grab of untreated influent during dosing without sampling (Table 5)	NA		4			4
Untreated stormwater grab						
Stormwater sample grab, delivered to KCEL immediately	T_0	--	1	0	1	0
Stormwater sample grab in Bioretention Laboratory at time of influent compositing	T_1	--	0	0	1	0
Stormwater sample grab upon arrival at KCEL after bioretention test	T_3	--	1[a]	0	1	0
Untreated stormwater composited into influent for treatment						
Composited stormwater influent in Bioretention Laboratory at time of compositing	T_1	--	3	0	3	3
Untreated stormwater composite, upon arrival at KCEL after bioretention test	T_3	--	0	0	1	0
At the point of toxicity testing	T_4	--	1	1	1	1
Treated stormwater						
Post treatment effluent, at the time of sample collection in bioretention laboratory	T_2	--	12	0	12	12[b]
Treated stormwater composites, upon arrival at KCEL after bioretention test	T_3	--	0	0	4	0
At the point of toxicity testing	T_4	--	4	3	4	4

Notes – FHM = fathead minnow (60/40 BSM final flush only); [a] – This 6PPD-Q sample to be both placed in amber glass and analyzed concurrent with toxicity test water. [b] – TSS only.

2.3 Project Objectives

The overall project objective is to execute the experimental design (next section) effectively. Sampling, sample handling, analysis and reporting objectives of this project are as follows:

- Set up the soil column experimental equipment, consisting of three replicate columns of each HPBSMx and of 60/40 BSM, in the Bioretention Laboratory. Conduct quality assurance (QA) steps and column preparation steps called for by the experimental design.
- Collect stormwater samples (as whole/untreated stormwater) from the selected location in Seattle (Figure 1) during three separate storm events. A successful stormwater sampling event will result in sample containers with a combined 455 liters (120 gallons) of stormwater runoff for use in the experiment.
- Measure, for each storm event, untreated stormwater from the stormwater source for 6PPD-Q. Concentrations are expected to be toxic to coho salmon (> 0.060 µg/L) prior to performing the bioretention media column tests. If sufficiently high concentrations are not present in the stormwater, be prepared to halt the tests for that storm and develop alternative plans.
- Transport stormwater to the Bioretention Laboratory for filtration through soil columns, perform column tests, and successfully collect effluents from each treatment type and untreated stormwater effluents at sufficient volumes for toxicity and chemical testing.
- Transport samples from the Bioretention Laboratory to KCEL in Seattle for analysis of 6PPD-Q and toxicity tests.
- Successfully track each sample and subsample through the process, collect data on water quality characteristics that may vary between storms and may vary because of bioretention treatment, and those that could affect treated effluent toxicity at designated sampling time points (Table 2).
- Complete all project QA steps and compile documentation necessary for QA review of results and inclusion of necessary data qualifiers.
- Prepare timely project reports to ensure experimental results are shared widely within the stormwater quality management community.

3.0 EXPERIMENTAL PROCESS AND TASKS

The experiment involves:

- Bioretention media column construction, preparation and flushing in the Bioretention Laboratory
- Stormwater sampling and sample transport (Appendix B)
- Performance of bioretention media column tests, including dosing with stormwater and sampling (dosing-with-sampling)
- Weathering of columns with stormwater without sampling for chemistry and toxicity tests (dosing-without-sampling)
- Chemical analysis and toxicity tests of both untreated stormwater and treated effluents
- Collection of data for water quality variables at designated time points during each storm cycle.

This section describes those procedures, in the general order that they will be performed. Later sections describe organizational structure and lines of communication, MQOs, data handling and data verification, validation, and management.

3.1 Bioretention Media Column Construction and Preparation

The Bioretention Laboratory Manager will obtain materials, and construct and prepare the bioretention media columns. Preparation includes a series of QA steps, which are outlined first in this section, followed by greater detail for each subsequent step.

3.1.1 Constructed Bioretention Media Columns – QA Steps

In the Bioretention Laboratory, the following QA steps will be performed:

6PPD-Q loss to equipment. 6PPD-Q may bind to the plastics in the bioretention media column testing equipment. To evaluate the importance of this to interpretation of experimental results, the first step is to evaluate the 6PPD-Q loss potential within the soil column equipment. To do this:

1. A single 20-liter sample consisting of DI water spiked with 6PPD-Q will be washed through the bioretention tanks, pumps and one column. The volume of spiked water used, and the equipment rinsed will be scaled to the final system for the actual tests; the equipment materials in this step will be the same as for the actual column test. The spiked water will be prepared by the Bioretention Laboratory. A 6PPD-Q analytical standard (HPC Standards, product #688152) of 100 µg/ml 6PPD-Q in acetonitrile will be used. 60 µL will be spiked into 20 L of WWU laboratory water to achieve approximately 3x the LC_{50} for the influent. The effluent will be analyzed for

6PPD-Q. Exact volumes of input and output waters will be measured. The difference in 6PPD-Q mass between the initial spiked sample and the output sample will be used to inform interpretation of 6PPD-Q loss from the BSM treatments later in the experiment. The result will be used to help characterize uncertainty about the efficacy of each bioretention treatment. Results will not be used to make quantitative adjustments during data interpretation. The equipment will be thoroughly rinsed following this step, and the column used will be included in the rinsate blank.

2. **Equipment rinse blank**. Following equipment preparation and before setting up soil columns, two column array equipment rinsate blanks will be collected. One rinsate blank will be collected on the single column used in the loss-to-equipment step above. A second rinsate blank will be from a subset of 3 of the actual and complete set of bioretention media columns. Both rinsates will include the mixing and storage tanks and conduit equipment. Each rinsate blank consisting of 20 L of DI water will be run through the system. The column used in the loss-to-equipment rinse will be run first and will not be included as one of the three columns in the rinsate blank. A third rinsate blank (1 L) will be performed on one of the 20-L carboys to be used to transport both stormwater samples and the treated effluent samples for toxicity testing. For each equipment rinsate blank, a single rinsate sample will be collected for analysis of 6PPD-Q. If the chemical is found above the method detection limit, the equipment will be rinsed extensively with tap water (at least 375 L) or replaced before the experiment begins. We do not expect that more than one rinsate blank will be necessary because the system is not expected to contain 6PPD-Q.

3.1.2 Test Column Materials

The Bioretention Laboratory Manager will purchase bulk mineral, bulk organic, and amendments necessary to blend the four media types described in Section 2.2. The conformance of media components with specifications for nutrient and copper leaching in Ecology's (2021) *Guidance on using new high performance bioretention soil mixes* will be demonstrated. Synthetic precipitation leaching procedure (SPLP) will be conducted on a grab sample of each media type (coir, sand and biochar) to be used in the bioretention media columns. Results of the SPLP will be used to ensure that the media components meet Ecology HPBSM specifications for maximum contaminant levels. Maximum contaminant levels from the media components are the following: Cu ≤10 µg/L; nitrate-nitrite ≤0.5 mg/L; ortho-phosphorus ≤0.15 mg/L; and TP ≤0.5 mg/L.

3.1.3 Basis for Influent Volume

The input water volume loaded to the bioretention media column array (or "hydraulic load") during preparatory flushing and experimental dosing is calculated to represent a specified bioretention design under specific rainfall assumptions. Our hydraulic load calculation is based on:

- Contributing area (CA) to bioretention facility surface area (FSA) ratio. Hydraulic load will be scaled to a CA/FSA of 15/1. This represents a facility area that is 6.7 percent of the area contributing stormwater to the system.
- Contributing area effectiveness (CAE) is set at 0.9. This represents the assumption that 90 percent of precipitation from the contributing area is delivered to the bioretention facility.
- Runoff treatment requirement (RTR) refers to the fraction of total stormwater volume that is required by Ecology to undergo treatment in a bioretention facility.
- Target precipitation depth (PD): 6.7 cm (2.64 inches) of precipitation. This is equivalent to the 10-year, 24-hour storm for the Seattle area.

With these considerations, hydraulic load, or input water volume, for both flushing and dosing steps is determined by the following (Equation 1):

Input water volume (L) =
column area (cm^2) x CA/FSA x PD (cm) x CAE x RTR/ 1000 (cm^3/L)

where: column area = 324 cm^2
contributing-to-facility area ratio (CA/FSA) = 15/1 (unitless)
contributing area effectiveness (CAE) = 0.9 (unitless)
RTR = 0.91 (unitless)
target precipitation depth (PD) = 6.7 cm

This calculation step informs both the flushing step and the dosing-with-sampling and dosing-without-sampling steps.

3.1.4 Test Column Construction and Flushing

The Bioretention Laboratory Manager will construct three columns for the four media types represented (Section 2.2). Media components meeting quality criteria (Section 3.1.2) will be combined into BSM blends, placed in polyvinyl chloride (PVC) columns, and flushed at the WWU Institute of Environmental Toxicology (see Figure 2 for a schematic of the column array).

3.1.4.1 Column Preparation

The proportions of BSM components in each blend will reflect those in Ecology-approved HPBSM systems. In each column with HPBSM or 60/40 BSM, a 30.5 cm (12-inch) polishing or drainage layer will be placed in the column first. This provides a filter before discharge through the under-drain pipe. The depth of the primary HPBSM and 60/40 BSM layer will be 45.7 cm (18 inches). The experimental column structure is 20.3 cm (8 inches) in diameter and 91.4 cm (36 inches) tall. The final project report will specify the sources and/or specific types of materials used in the HPBSM and 60/40 BSM components (e.g., species of wood for the high carbon wood ash biochar) used.

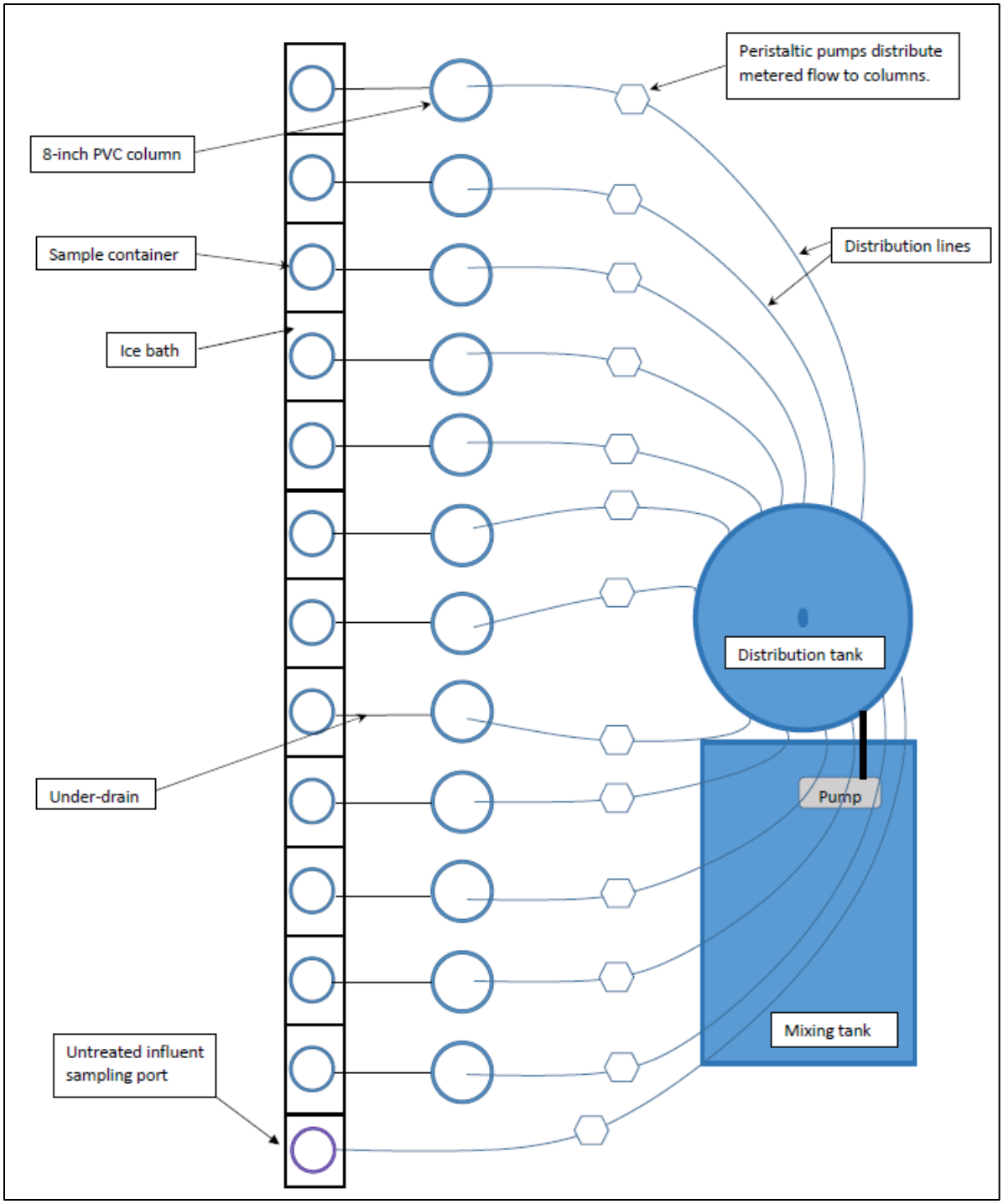

Figure 2. Schematic of Column Array

3.1.4.2 Column Flushing

Following set up of bioretention media columns, the columns will be flushed with the equivalent of 14 storm cycles using DI water. The purpose of this flushing is to ensure that BSM constituents do not generate contaminated effluents. Each flush will be conducted with 27 liters of DI water per column. DI water used for the flushing influent will be assumed as below reporting limits for TSS (1.0 mg/L), total phosphorus (0.008 mg/L), ortho phosphorus (OP; 0.004 mg/L, nitrate-nitrite (0.1 mg/L), dissolved copper (2.0 µg/L), and dissolved zinc (2.5 µg/L).

After the first and the last of the prescribed series of flushing steps (Table 3), samples of the flush-water will be collected. Sample collection for chemical analyses and toxicity testing will commence after the entire modeled storm volume for each treatment has been collected.

Table 3. Flushing Regime

Flushing Event	Day	Volume Applied (liters/column)	Equivalent Storm Size (cm)	Cumulative Rain (cm)	Cumulative Rain (inches)	Percent Water Year Seattle
Flush 1 Sample 1	1	27	6.7	6.7	2.6	7
Flush 2	3	27	6.7	13.4	5.3	15
Flush 3	5	27	6.7	20.1	7.9	22
Flush 4	7	27	6.7	26.8	10.6	29
Flush 5	9	27	6.7	33.5	13.2	37
Flush 6	11	27	6.7	40.2	15.8	44
Flush 7	13	27	6.7	46.9	18.5	51
Flush 8	15	27	6.7	53.6	21.1	59
Flush 9	17	27	6.7	60.3	23.7	66
Flush 10	19	27	6.7	67.0	26.4	73
Flush 11	21	27	6.7	73.7	29	81
Flush 12	23	27	6.7	80.4	31.7	88
Flush 13	24	27	6.7	87.1	34.3	95
Flush 14 & Sample 2	25	27	6.7	93.8	36.9	103

Flush water volume. Hydraulic load (input water volume) for the flushing phase was calculated as described above (Section 3.1.3). For the flushing phase:

- Target precipitation depth for flushing: 6.7 cm (2.64 inches).
- Per column flushing volume: approximately 27 liters per flushing event.

Event duration. For the flushing process, 27 liters per column will be delivered during each flushing event at a pump rate of 11.0 liters per hour for approximately 2.5 hours.

Drain down. Columns will be allowed to drain down for a minimum of 12 hours between flushing events.

Flush water sampling. Flush water effluents from each of the three replicate bioretention media columns will be composited into one sample per bioretention treatment type. From each composite, 2.5 L will be required for metals and conventionals chemistry (see Table 10 for sample volumes). These will be analyzed for TSS, DOC, dissolved and total cadmium, copper, lead, and zinc, and total calcium and magnesium; and pH will be measured (Table 4).

Following the final flush, samples of composited effluent from each treatment type will also be analyzed as follows:

- 2 L for fathead minnow[2] toxicity testing (60/40 BSM only, N=1)
- 0.25 L for analysis of 6PPD-Q (N=4).

The flushing process will be repeated until 6PPD-Q is below the MDL in the flush waters, all other measured chemical constituents are below reported acute toxicity thresholds for fish (Table 4), and effluent from the 60/40 BSM is not acutely toxic to fathead minnow..

Table 4. Selected Analytes to be Tested in Flush Water

Analyte	Target Concentration (low)	Target Concentration (high)
6PPD-Q	< MDL (0.01 µg/L)	< MDL (0.01 µg/L)
Total Suspended Solids	75 mg/L	200 mg/L
pH	no target	no target
Dissolved Organic Carbon	no target	no target
Total Cd	0.25 µg/L	no target
Dissolved Cd	0.1 µg/L	no target
Total Cu	20 µg/L	50 µg/L
Dissolved Cu	7.0 µg/L	20 µg/L
Total Pb	no target	no target
Dissolved Pb	no target	no target
Total Zn	150 µg/L	500 µg/L
Dissolved Zn	50 µg/L	300 µg/L

[2] The final flush water from only the default 60/40 BSM will be tested for toxicity to fathead minnow as a preparation step for the experiment. Flush water from other treatment types will not be subject to this test. We take this approach because leachate from default 60/40 BSM has previously been shown to contain levels of copper greater than Washington water quality standards for the protection of aquatic life. The other HPBSMx to be tested have been shown not to leach metals, and any metals from the compost in Type 3 are removed by the primary and polishing layers.

3.1.5 Stormwater Sampling and Sample Transport

Stormwater runoff from Seattle will be collected at the location in Figure 1 during three separate storms. The Field Lead is responsible for tracking weather forecasts and communicating with the Project Team in time to allow full preparation for the sampling and analysis series following each stormwater sampling event (see Section 6.2).

To prevent clogging of equipment at the Bioretention Laboratory with suspended matter, storms with an antecedent dry period (0 – 0.05 inchesof rain) of up to 2 days will be preferred, to minimize time for accumulation of dirt and organic debris that will be transported in stormwater. Each stormwater sample will be collected directly from stormwater that drains the I-5 bridge over Lake Union in Seattle and nearby residential area. The site is often used in stormwater BMP technology evaluations. Stormwater will be drained from the stormwater source via an established sampling point with a valve. A volume of 455 L will be collected in 23 fluorinated 20-L high density polyethylene (FHDPE) carboys for transport to the Bioretention Laboratory. A grab sample will also be collected as described below. The head space (open air at the top of each sample container) in each sample container will be minimized in all samples to avoid mixing oxygen into the sample during transportation.

For transport to the Bioretention Laboratory, each 20-L carboy will be placed in an open container and surrounded by bagged ice; the container holding the carboys will not be sealed shut. Samples will be covered with a black tarp or similar and maintained in the dark during holding and transport.

At the Bioretention Laboratory, the set of 20 L stormwater samples will be combined into a mixing tank and composited. To composite the subsamples, stormwater will be stirred in the mixing tank by stainless steel propeller and pumped to a distribution tank (Figure 2).

In addition, at the time stormwater sampling is conducted (time of field collection, or T_0, Table 2), a stormwater grab sample will be collected and split into three aliquots:

- One 0.3 to 0.5 L aliquot will be placed in a container with a wide mouth opening. Water quality characteristics will be measured and recorded.
- The second 0.25 L aliquot will be collected in an amber glass container and delivered to KCEL for analysis of 6PPD-Q or storage at ≤4°C until analysis.

The remaining volume of this 2L grab stormwater sample will be transported to the Bioretention Laboratory. It will be transported in a 2 L FHDPE container and with the stormwater sample for treatment, at the same temperature. This sample will undergo periodic measurement of water quality characteristics, and analysis for 6PPD-Q at the end of the cycle (Table 2; Appendix B).

3.2 Dosing Bioretention Media Columns

Dosing the bioretention media column includes both dosing-with-sampling and dosing-without-sampling (Table 5). The volume of water used in each dose is calculated as described in Section 3.1.3. The precipitation depth for the bioretention media column dosing was selected as a loading rate that provides a rigorous test for the BSM and approximately 81% Seattle water year (or 73.7 cm [29 inches]) within the time frame of the study.

3.2.1 Dosing-with-Sampling

Following flushing, the bioretention media columns will be dosed with stormwater obtained as described in Section 3.1.5. The composited stormwater influent will be sampled in 3 discrete samples of influent per storm using the influent sampling port (Figure 2), as described below.

3.2.2 Dosing-without-Sampling

In addition to dosing the columns with stormwater from three separate storms, bioretention media columns will be dosed between storms, but with no sample collection (Table 5). The purpose of dosing-without-sampling is to simulate the bioretention facility weathering process in the test columns and improve the realism of results. Improving the realism will generate results that better represent a field condition for 6PPD-Q control. The equivalent of four additional storms, with stormwater volume of 27 L per column (Table 5) will be run between each dosing-and-sampling event.

Table 5. Stormwater Dosing Regime

Dosing Event	Volume Applied	Equivalent Storm	Cumulative Rain		Percent
	(liters/column)	(cm)	(cm)	(inches)	Water Year (Seattle)
Dose / Sample 1	27	6.7	6.7	2.6	4
Dose 2	27	6.7	13.4	5.3	15
Dose 3[a]	27	6.7	20.1	7.9	22
Dose 4	27	6.7	26.8	10.6	29
Dose 5 [a]	27	6.7	33.5	13.2	37
Dose 6 / Sample 2	27	6.7	40.2	15.8	44
Dose 7 [a]	27	6.7	46.9	18.5	51
Dose 8	27	6.7	53.6	21.1	59
Dose 9 [a]	27	6.7	60.3	23.7	66
Dose 10	27	6.7	67	26.4	73

Dosing Event	Volume Applied	Equivalent Storm	Cumulative Rain		Percent
	(liters/column)	(cm)	(cm)	(inches)	Water Year (Seattle)
Dose 11 / Sample 3	27	6.7	73.7	29	81

Notes
[a] – Influent water will be sampled for 6PPD-Q, DOC and TSS.

For efficiency, stormwater for the dosing-without-sampling will be collected by the Bioretention Laboratory Manager from a location in Bellingham, Washington. Stormwater to be used for this purpose will be collected from a wet/detention pond built in 2005 using the WSDOT 2005 Hydraulic manual and the WSDOT 2004 Highway Runoff Manual when the average daily traffic was calculated at 6,430 vehicles. At the time, this was below the threshold for requiring enhanced treatment. The pond is designed to treat 100% of stormwater runoff from approximately 1 acre of impervious surface, and 1/3 of an acre of pervious land cover for water quality and water quantity. The drainage area consists of a mix between southbound I-5 lanes, the eastern half of the southbound on-ramp at Connelly Avenue in Bellingham, and the southern half of Connelly Avenue/I-5 underpass, plus the grass embankment between the on-ramp and southbound lanes of I-5. Stormwater flows through an enclosed system directly to the pond without any additional treatment. This dosing-without-sampling stormwater will be sampled from the "untreated influent sampling port" (Figure 2) during Dose 3, Dose 5, Dose 7 and Dose 9 for 6PPD-Q (0.25 L, amber glass), DOC (0.125 L, amber glass) and TSS (1 L HDPE) .

Results of sampling the stormwater collected in Bellingham for the dosing-without-sampling will be used to characterize (qualitatively) the representativeness of a Seattle water year at the end of the study. For example, if the 6PPD-Q in these samples is consistently below detection limits, or TSS and DOC are much lower than in dosing with sampling stormwater, reporting could clarify that results might be different than if Seattle stormwater was used in this step. If these constituents are at levels comparable to the dosing-with-sampling (Seattle)_stormwater, then reporting will express confidence that an 81% Seattle water year is represented.

3.2.3 Stormwater Dose Volume

Input water volume, or hydraulic load, for each dosing event is calculated as described in Section 3.1.3 and represents approximately 81% Seattle water year within the time frame of the study. The following target precipitation depth, volumes, and pump rates are planned:

- Target precipitation depth for all dosing steps: 6.7 cm (2.64 inches) equivalent precipitation.
- Dosing volume for all dosing experiments: Approximately 27 liters per column per sampling event.
- Column drain down: minimum of 12 hours between dosing experiments.

- Sampling event duration: For all dosing events 27 L will be delivered at a pump rate of 11 liters per hour for approximately 2.5 hours.
- For all four treatments, a ~ 22 L sample will be collected from each effluent line, and subsampled, as described below (Section 3.2.5).

The additional 5 liters of delivered stormwater/column is anticipated to be retained in the media pore space.

3.2.4 Influent Water Sampling

Thirteen distribution ports are placed at the bottom of the distribution tank (Figure 2). Twelve ports will distribute flow, by peristaltic pump, to the HPBSM and 60/40 BSM columns and the thirteenth will discharge directly to a sampling station. At this sampling station, the following influent water samples will be collected:

- A series of three 0.25 L samples of influent for analysis of 6PPD-Q, using amber glass containers
- A series of three 1 L samples of influent for analysis of TSS
- A series of three 0.125 L samples for DOC.
- A series of three 0.3 to 0.5 L for measuring water quality characteristics. These will be discarded after measurements are taken.
- A single 20 L sample will be collected for use in water quality measurements upon receipt at KCEL, 6PPD-Q analyses, and toxicity tests with coho, in a clean, 20-L fluorinated FHDPE carboy.

Head space will be minimal in filled sample containers. The three discrete 0.25 L samples of influent for 6PPD-Q analysis and the toxicity test sample will be placed on ice and maintained in the dark for transportation to KCEL.

3.2.5 Effluent Water Sampling

To sample effluent following each of the three dosing-and-sampling events (Table 5) effluent water from each of the individual columns will be collected in 24.6-liter glass containers placed in a tub of ice.

The following samples of effluent will be collected:

- From each of the three columns within a bioretention media type, 0.25 L aliquot of effluent from each column will be reserved for analysis of 6PPD-Q (N=12 effluent samples per storm). A 1 L aliquot will be collected for analysis of TSS, and 0.125 L will be collected for analysis of DOC.

- From each of the three columns for each bioretention media type, a third aliquot of 0.3 - 0.5L effluent from each column will be immediately tested for the water quality characteristics, and results will be recorded[3].

  From each of the three columns of each bioretention media type, a ~6.6L effluent sample will be collected; all three from each BSM type will be composited into a single ~20 L water sample, homogenized, and transported to KCEL.

  When this sample arrives at KCEL:
  - 0.3 L sample from each effluent composite for each bioretention media type will be placed in a beaker and water quality characteristics will be recorded.

  At the time of toxicity testing, the remaining ~20 L for each bioretention media type will be used in water quality measurements, 6PPD-Q analyses, and the acute toxicity test with coho[4]. It will be subsampled as follows:
  - 0.25 L aliquot will be tested for 6PPD-Q
  - 1 L aliquot will be tested for TSS
  - 0.125 L aliquot will be tested for DOC.

All effluent samples will be maintained in the dark and at ≤ 4°C during transportation and storage.

3.3 Toxicity Testing and Chemical Analysis

Toxicity tests will be performed according to the EPA (2002), *Methods for measuring the acute toxicity of effluents and receiving waters to freshwater and marine organisms*, and EPA Test Methods 2019.0 and 2000.0. Analytical chemistry for 6PPD-Q will be performed according to KCEL's analytical method for 6PPD-Q. The 6PPD-Q analytical method is in review by Ecology and pending approval. QA specifications for toxicology and chemistry related to this project are presented in later sections of this QAPP. Procedures for handling and management of treated effluent samples by KCEL are briefly described below.

3.3.1 Toxicity Testing

Two types of fish acute toxicity tests will be performed.

3.3.1.1 Fathead Minnow

One 2-L sample of flush water from the 60/40 BSM column following the final flush will be tested for acute toxicity to fathead minnow as part of preparation of the bioretention media columns. The fathead minnow test will be conducted according to EPA Test Method 2000.0: Fathead Minnow, *Pimephales promelas*, Acute Toxicity Tests with Effluents and Receiving Waters and KCEL standard operating procedure (SOP) #414v3.

[3] Measuring water quality parameters of effluent samples may not require a separate vessel. If the probes fit into the glass containers with effluents, water quality parameters will be measured directly in the effluent sample container.

[4] Except Type 2; effluent from HPBSM Type 2 will not undergo toxicity tests.

3.3.1.2 Coho Salmon

Toxicity tests with coho will be conducted on effluent composited from the 60/40 BSM, Type 1 and Type 3 HPBSM, untreated stormwater, and a laboratory control (laboratory well water).

In general, the tests will follow these procedures:

- **Species:** Toxicity tests will be performed using juvenile coho salmon, obtained as embryos from Issaquah Hatchery and reared in KCEL's Aquatic Toxicity Laboratory.
- **Replication**: four exposure chambers per treatment will be used, with five individuals per chamber.
- **Exposure duration:** Toxicity tests will be 24 hours duration
- **Test endpoint**: 1) the number of dead fish per replicate following 24 hours exposure will be recorded, 2) observational notes of suspected URMS symptoms (disorientation, swimming in circles, gaping, etc.) will be made in the first 12 hours of exposure.
- **Water quality control**: standard test parameters for acute fish toxicity tests include DO, pH, temperature, conductivity, ammonia (unionized calculation), alkalinity and hardness in toxicity test chambers, to be measured according to the EPA Test Method 2019.0. This monitoring is to ensure the basic water quality in test chambers is not the cause of acute mortality. In addition, the water quality characteristics (ORP, conductivity) will be recorded in each composited effluent prior to conducting the toxicity test.

  Both types of tests will include an influent sample and a negative (laboratory water) control sample.

3.3.2 Chemical Analyses

DOC will be analyzed by KCEL SOP #3036 and SM 5310-B. DOC samples are first filtered through a 0.45 µm filter.

TSS will be determined by KCEL SOP #3009 and SM 2540-D. For the determination of TSS, a measured volume of a well-mixed sample is filtered through a glass fiber filter. The residue retained on the glass fiber filter is dried to a constant weight at 103-105°C. The resulting net weight represents the total suspended solids.

6PPD-Q will be quantified by liquid chromatography/triple quadruple mass spectrometry using an isotopically-labeled internal standard (D_5-6PPD-Q) method as in Hunt et al. (2021) as documented in KCEL SOP# 4077v0.

A more detailed description of MQOs for all analytical endpoints (Section 5) and toxicity test and chemistry methods (Section 7) are in later sections of this QAPP.

3.4 Stormwater Water Quality Characteristics

At various points throughout the experimental cycle performed for each storm (Table 2), information on the stormwater quality characteristics that may be affected by bioretention media or other factors will be collected (Table 2). Results will describe how bioretention and the sample handling process affects each one.

At each point during an experimental cycle that water quality characteristics are collected, an aliquot of up to 0.3 to 0.5L of the water to be tested will be put into a wide mouth container. One or more single- or multi-parameter probes will be used to measure the following characteristics:

1. Temperature (°C), SOP #245v1
2. Specific conductance (or conductivity) (mS/cm), SOP #245v1
3. pH (unitless), SOP #245v1
4. Oxidation-reduction potential (mV), Hanna H198190 user manual
5. Dissolved oxygen (mg/L), SOP #245v1

Data collection will be performed in accordance with the KCEL Field Sciences Unit's (FSU's) SOPs for field measurement of each of these parameters. A multiparameter probe will be used for temperature, pH, specific conductance and DO; the appropriate SOP will be applied (e.g., Attended YSI EXO Multiprobe Operations, SOP# 245v1 2017). For ORP measurements, a standalone field meter will be used. All calibration procedures, recordkeeping and instrument use will be consistent with SOPs or manufacturer's instructions if SOPs are not available. Final decisions on use of specific probes and procedures will be documented in a Field Procedures Report.

3.5 Assumptions and Contingencies

The study design includes inherent assumptions, and contingency plans:

- The stability of 6PPD-Q in the stormwater matrix is unknown. KCEL is currently conducting a holding time study to evaluate its stability in stormwater. The King County Project Manager will be informed of the results, and results will be included in the project report to Ecology. Every effort will be made to conduct the 6PPD-Q analysis within this evaluated holding time. The Project Team intends to move quickly to minimize the time needed to perform the work for each storm cycle, and to keep samples cold to prevent degradation. In addition, we will test several water quality characteristics throughout the process to follow changes in each parameter over time required to conduct all steps during each storm event.
- 6PPD-Q concentrations will be sufficiently high in stormwater samples to be potentially toxic as influent to HPBSMx and 60/40 BSM treatments. KCEL is currently working to characterize the 6PPD-Q concentrations in stormwater from the sampling location. If this characterization shows 6PPD-Q concentrations will not

be reliably above 0.1 ug/L, KCEL will develop a contingency plan that will consider options such as supplemental spiking of stormwater with 6PPD-Q and/or sampling an additional storm event.

- Coho hatching and development may not be completed by the target start date of February 15. The Project Team addresses this contingency as follows:
    - The stormwater sampling location is likely to provide sufficient volume of stormwater even in relatively mild rainfall events (1 – 2 cm). This increases the likelihood that 3 successful sampling events will take place during the available time
    - 6PPD-Q will be measured directly, which will still allow the Project Team to achieve DQO-1 (Appendix A), and to achieve the primary goal of the project (Section 2.1), even if coho toxicity tests cannot be performed.
    - Based on results of pending holding time study, samples may be frozen or held at ≤4°C until coho are ready for testing.

Violation of one or more of these implicit assumptions will not jeopardize the project.

4.0 ORGANIZATION AND SCHEDULE

This project is a collaborative effort between King County Science and Technical Services Section, the King County Environmental Laboratory, and Curtis Hinman and Associates. Western Washington University is providing a facility for the Bioretention Laboratory.

4.1 Key Individuals and Responsibilities

Table 6 summarizes staff involved in this project and responsibilities of each person.

Table 6. Organization of Project Staff and Responsibilities

Title	Name	Affiliation	Responsibilities
Ecology Project Manager	**Morgan Baker** Water Quality Program, Ecology **Phone**:(360) 706-4079	Washington Dept. of Ecology	Clarifies scope of the project. Provides internal review of QAPP and approves final QAPP.
Ecology Quality Assurance Officer	**Brandi Lubliner** Water Quality Program, Ecology **Phone**:(360) 407-7671	Washington Dept. of Ecology	Reviews/approves draft QAPP and final QAPP.
King County Project Manager	**Jenée Colton** King County, Dept. of Natural Resources & Parks, Water & Land Resources Division **Phone**: (206) 477-4075	King County Science and Technical Services Section	County grant contract management. Contact person for Ecology. Oversees QAPP and development of other deliverables development, and project execution. Responsible for project execution, reporting and billing.
King County Technical Lead	**Jennifer White** King County, Dept. of Natural Resources & Parks, Water & Land Resources Division **Phone (M)**: (206) 572-5506	King County Science and Technical Services Section	Drafts QAPP, coordinates logistics and technical details with Bioretention Laboratory Project Manager and KCEL to plan and implement study; interpret study results and drafts deliverables to Ecology, coordinates internal reviews, finalizes report for Ecology.
Bioretention Laboratory Project Manager	**Curtis Hinman** Curtis Hinman and Associates Bellingham, WA 98225 **Phone**:(253) 330-9878	Curtis Hinman and Associates	Prepares and manages Bioretention Laboratory and student technicians. Performs all QA steps required. Oversees bioretention media column test process and sample collection within the laboratory. Responsible for preparing laboratory report.
KCEL Aquatic Toxicology Lead	**Fran Sweeney** King County, Dept. of Natural Resources & Parks, Water & Land Resources Division **Phone**: (206) 477-7117	King County Environmental Laboratory	Manages and oversees Toxicology Laboratory and laboratory scientists. Performs all QA steps and documentation. Responsible for preparing toxicology laboratory report.
KCEL Laboratory Project Manager	**Susannah Rowles** King County, Dept. of Natural Resources & Parks, Water & Land Resources Division **Phone:** (206) 477-7158	King County Environmental Laboratory	Manages and oversees laboratory analyses, coordinates with lab units. Responsible for preparing chemistry laboratory report.

Title	Name	Affiliation	Responsibilities
Laboratory Project Manager	Kelley vanHees Water Chemistry Department Ferndale, WA **Phone**: (360) 733-1205	Exact Scientific Services, Inc.	Manages and oversees laboratory for analysis of flush water. Ensures performance of all QA steps, documentation and reporting. Responsible for preparing laboratory report.
King County Field Lead	**Christopher Barnes** King County, Dept. of Natural Resources & Parks, Water & Land Resources Division **Phone**: 206-477-7143	King County Environmental Laboratory, Field Sciences Unit	Tracks weather and identifies storms for sampling, informs team as weather certainty improves, performs and oversees sample collection and sample transport between Seattle and Bellingham.

4.2 Proposed Project Schedules

Project schedules are needed for the overall project as well as each storm cycle. Each is summarized below.

4.2.1 Project Schedule

Target schedule milestones to guide execution of this study are summarized in Table 7. Specific preparation steps to be complete by February 30, 2023 include:

- Ecology-approved QAPP is complete and final
- Bioretention Laboratory is fully set up, flushing steps complete, results for chemistry and toxicity of final flush water are complete.
- Toxicology and chemistry laboratories are prepared with equipment, access to test organisms (an adjustment to start date may be needed based on coho development).
- Field equipment is purchased, prepared and available for use.

Table 7. Project Milestones

Task	Due date
Ecology-approved QAPP complete and final	February 15, 2023
All laboratories prepared	
All stormwater testing cycles complete	April 31, 2023
Assembly of laboratory and field reports	May, 2023
Submittal of Project Report to Ecology	June 25, 2023
Data interpretation and report assembly	Summer, 2023
Final Interpretive Report complete	September 30, 2023

4.2.2 Storm Cycle Schedule

The schedule for performance of the experiment for each storm will be as short as possible.

Schedule drivers

- Stormwater samples can be collected Monday through Thursday. This leaves a second day during any storm cycle that may be necessary for toxicity tests.
- Antecedent dry period (the number of days with dry weather 0 to 0.05 inches of rain that precede a sampled storm) should be 0 to 2 days. This is necessary to prevent clogging the bioretention media columns with suspended matter.

Storm Test Cycle

Below is the approximate schedule for a storm cycle.

Day 1

- Collect stormwater sample in Seattle and immediately transport to Bellingham[5]
- Deliver stormwater grab sample to KCEL
- Delivered stormwater sample to Bioretention Laboratory, immediately start compositing and column test
- Complete all effluent sample collections, and measurements, and composites in Bioretention Laboratory, transport samples to KCEL in Seattle.
- Log in all samples at KCEL[6], water quality conditions are measured in effluent composites, and samples are stored at ≤ 4°C overnight.

Day 2

-
- Initiate toxicity tests.

Sample toxicity test influent and effluent samples; analyze within the 6PPD-Q holding time.Day 3

- Complete toxicity tests.

Between Storm Cycles

The time between storm cycles is a minimum of 1 week. During this time:

- The Bioretention Laboratory will perform weathering cycles and arrange for cleaning of vessels used for effluent collection by Exact Scientific.
- The Field Team will clean sampling equipment, perform troubleshooting and replenish equipment and supplies.

[5] If the stormwater collection cannot be completed by 11 AM due to the storm conditions, the stormwater will be stored at KCEL and the rest of the Day 1 schedule will commence on the following day.
[6] Login may occur on Day 2.

5.0 QUALITY OBJECTIVES

This experiment does not have specified regulatory or other standards that determine analytical requirements. Quality objectives for this project are defined by those of the laboratories involved and requirements of their internal method protocols (Appendix C), and by the KCEL's 6PPD-Q method, as summarized in this section.

5.1 Data Quality Objectives

The DQOs for this project were prepared consistent with EPA's seven step DQO process (USEPA 2006) and are presented in Appendix A.

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 MQOs for Precision, Bias, 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. Precision, bias and sensitivity MQOs for 6PPD-Q, TSS and DOC, to be analyzed by KCEL; and MQOs for target analytes in flush water to be analyzed for Exact Scientific are described in Table 8. Collection of data on the water quality characteristics will be conducted using portable single- or multiparameter probes. MQOs for water quality characteristics are summarized in Table 9.

Table 8. Measurement Quality Objectives for Water Quality Analytes

Parameter	Method	Reporting Limit	Method Detection	Units	Method Blank	Spike Blank	Laboratory Duplicate	Matrix Spike	Matrix Spike Duplicate
		Limit	Limit			% Recovery	RPD[a]	% Recovery	RPD[a]
6PPD-Q	KCEL SOP# 4077	0.05[4]	0.01[4]	µg/L	<MDL	50-150	40	50-150	45
Total suspended solids (KCEL)	SM2540D	1	0.5	mg/L	<MDL	NA	25	NA	NA
Total suspended solids (Exact Scientific)	SM2540D	1	1	mg/L	<RL	90-110	<10%	N/A	N/A
Dissolved organic carbon (KCEL)	SM5310B	1	0.5	mg/L	<MDL	80-120	20	75-125	NA

Parameter	Method	Reporting Limit	Method Detection	Units	Method Blank	Spike Blank	Laboratory Duplicate	Matrix Spike	Matrix Spike Duplicate
		Limit	Limit			% Recovery	RPD[a]	% Recovery	RPD[a]
Dissolved organic carbon (Exact Scientific)	SM5310C	0.5	0.1	mg/L	<MDL	90-110	<10	70-130	NA
Cadmium, dissolved	200.8	0.1	0.1	µg/L	<RL	90–110%	<10%	70–130	≤20% or ±2 x RL
Cadmium, total		0.25[2]	0.06[2]				<10%		
Calcium	200.8	0.15	0.076	mg/L	<RL	90–110%	<10%	70–130	≤20% or ±2 x RL
Copper, dissolved	200.8	2	--	µg/L	<RL	90–110%	<10%	70–130	≤20% or ±2 x RL
Copper, total			0.5				<10%		
Lead, dissolved	200.8	0.1	--	µg/L	<RL	90–110%	<10%	70–130	≤20% or ±2 x RL
Lead, total		0.5[2]	0.06[2]				<10%		
Magnesium	200.8	0.02	0.01	mg/L	<RL	90–110%	<10%	70–130	≤20% or ±2 x RL
Zinc, dissolved	200.8	2.5	--	µg/L	<RL	90–110%	<10%	70–130	≤20% or ±2 x RL
Zinc, total		20[3]	10				<10%		

Notes

[1] No field duplicates will be collected for this project.
[2] Can report between PQL and MDL with a qualifier.
[3] For zinc, the reporting limit (RL) is 20 µg/L. If the initial sample result is below the RL, it may be sent to a separate laboratory to quantify at or below 5ug/L.
[4] 6PPD-Q with 100X SPE the MDL is 0.0001 µg/L and RDL 0.0005 µg/L.

RL – reporting limit
RPD – relative percent difference

Table 9. Measurement Quality Specifications for Water Quality Characteristics

Parameter	Measurement Units	Range	Resolution	Accuracy
pH	standard units	0 to 14	0.01	±0.1 pH units when within ±10°C of calibration; otherwise ± 0.2.
Specific Conductance	mS/cm	0 to 200 mS/cm	Range dependent: 0.0001 to 0.01 mS/cm	0 to 100 mS/cm, ± 5% 100 to 200 mS/cm, ± 1%
Oxidation Reduction Potential	mV	± 2000 mV	0.1 mV	± 0.2 mV
Dissolved Oxygen	mg/L	0 to 50 mg/L	0.01 mg/L	0 to 20 mg/L, ±1% 20 to 50 mg/L ±5%
Temperature	°C	-5 to +50 °C	0.001 °C	-5 to +35 °C, ±0.01 °C +35 to + 50°C, ±0.05 °C

Precision

Precision is a measure of the repeatability of a set of replicated results and represents random error in the measurement process.

Laboratory analytical measurements: Targets for acceptable precision in terms of relative percent difference (RPD) or relative standard deviation (RSD), in Table 8.

Real-time measurements: Measurement of the water quality characteristics will take place in the field and in the laboratory, using standard single- or multi-parameter probes. The precision of each probe and measurement type is described in Table 9.

Bias

Bias is the systematic or persistent distortion of a measurement process which makes the result non-representative of the true value. Errors of bias in both laboratory analytical measurements and real-time measurements are minimized through use of standardized procedures by properly trained staff.

Laboratory analytical bias will be assessed the analysis of blanks, including method blanks, and instrument blanks (Table 8). Targets for bias are as listed.

- An equipment blank will be prepared by rinsing DI water through the bioretention media columns prior to loading with bioretention media and analyzing rinsate for 6PPD-Q (Table 2), prior to beginning the experiment.
- A bottle rinsate blank will be prepared by rinsing a carboy like those to be used to collect and transport stormwater samples to the Bioretention Laboratory prior to their first use and analyzing rinsate for 6PPD-Q (Table 2) prior to beginning the experiment.

- Method (or laboratory) blanks are prepared in the laboratory and processed in the same manner as the field samples and can, thus, provide information on the preparation process.

Real-time measurements: The Project Team will avoid bias in measurement of the water quality characteristics by performing calibrations according to the instrument specifications. All calibration records will be retained for the project record.

Sensitivity

Sensitivity is measured through reporting limit performance (for example, in a regulatory setting, the MDL is often used to describe sensitivity). Method detection limits and reporting detection limits will be provided with each analytical data report. Sensitivity of water quality measurements is determined by the resolution of the instruments used (Table 9).

5.2.1.1 MQOs for Representativeness, Comparability, 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., binding) of targeted analytes to experimental equipment, transformation of target compounds 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.

Representativeness

The sampling to be conducted for this project will generate stormwater from one location representing stormwater discharge of roadway runoff from an interstate highway. Dosing-without-sampling will also likely use interstate highway runoff. The resulting chemical dataset for untreated stormwater is expected to be representative of this specific river-roadway-storm event combination to be sampled. Results will not provide the basis for evaluating temporal variability of 6PPD-Q within a sampling location, other than across the three storm systems sampled in 2023.

Bioretention media columns will be set up to represent field conditions to the maximum extent possible and scaled to a bench scale, and consistent with other bench-scale studies of this type. Each stormwater dose to each bioretention media column is scaled to be equivalent to the 10-year, 24-hour storm for the Seattle area (Section 3.1.3); and the dosing regime will represent 81% of a Seattle water year (Table 5).

Flushing. Flushing ensures that loosely bound materials within the BSM used and that would not be anticipated in an *in situ* bioretention facility are absent prior to initiation of

dosing. The absence of toxic concentrations of metals and other constituents (Table 4) ensures that results of toxicity tests more likely represent functional bioretention systems.

Dosing. The bioretention media column array will be dosed and sampled (dosing-with-sampling) with three storms. Supplemental dosing-without-sampling increase the dosing events to 11 storm events. The inclusion of additional dosing events represents delivery of cumulative water volumes to each column of 81% of one Seattle water year for each of the BSM columns. Increasing the dosing in this manner brings greater realism and representativeness to the results. Improved realism improves applicability of data to stormwater quality management.

Comparability

Analytical results may be used in comparisons to 1) each other, among samples collected for this program, 2) results of similar surveys reported in the past or future by other local agencies or in the peer reviewed literature, 3) results of future surveys by King County, and 4) results of studies that document thresholds of potential toxicity to fish and other aquatic life. The primary means to ensure the project meets these comparability requirements is through the use of SOPs (Appendix C) and standard methods. SOPs to be employed during this project include:

Laboratory analytical procedures

- KCEL SOP #4077: 6PPD-quinone by LCMS/MS
- KCEL SOP #406v3 Rainbow Trout Acute Toxicity Test (modified for coho, Table 12)
- KCEL SOP #414v3 Fathead Minnow Acute Toxicity Test (flush water from 60/40 BSM only)
- TSS will be determined by KCEL SOP #3009 and SM 2540-D.
- DOC will be analyzed by KCEL SOP #3036 and SM 5310-B.

Real time measurement of water quality characteristics:

- Temperature (°C), SOP #245v1
- Specific conductance (or conductivity) (mS/cm), SOP #245v1
- pH (unitless), SOP #245v1
- Oxidation-reduction potential (mV), Hanna H198190 user manual
- Dissolved oxygen (mg/L), SOP #245v1

Copies of SOPs will be provided on request.

Additional steps that ensure comparability for the purposes listed above:

- Retained a commercial analytical laboratory for analysis of bioretention media column flush water with knowledge and experience in development and application of the analytical methods performed consistent with industry practice and standard methods.

- Established sample handling protocols. Field personnel will consistently follow required sample handling protocols for the target analytes (Table 10).
- Assembled an experienced Project Team to plan and execute the program in a manner that minimizes interference from exogenous contamination, prevents and tracks potential chemical degradation during handling, and various other errors that can occur during execution of water sampling projects.

Completeness

For this study to be successful, stormwater runoff at the designated sampling location (Figure 1) from three discrete storms will be collected. All steps listed in Section 3 will be successfully completed for each of three storms. Either the chemical analysis for 6PPD-Q, or toxicity tests, or both will be performed to provide an accurate representation of post-treatment and toxicity tested stormwater for all three storms. Achieving the Project Objectives (Section 2.3) will assure completeness.

5.3 Acceptance Criteria, Quality of Existing Data

This study builds on prior investigations of bioretention media effectiveness and performance in reducing the lethal toxicity of stormwater to coho salmon but does not rely on those prior investigations. Therefore, we have not established acceptance criteria for the existing data to be used in interpreting and reporting results for this study.

6.0 FIELD PROCEDURES

An overview of field sampling is presented in this section, and details are provided in Appendix B.

6.1 Invasive Species Evaluation

Washington law prohibits the transportation of all aquatic plants, animals, and many noxious weeds. For this project, there is no such risk. Samples will be collected at the end of a stormwater conduit. Related activities of field personnel will not risk spread of invasive species.

6.2 Sampling Procedures

The Field Lead will monitor weather forecasts to identify storm events to potentially be sampled. The following are the criteria to be met for a storm to be considered for sampling:

- Target storm events will be those forecasted to result in at least 0.6 cm (0.25 inch) of rain in a 12 -hour period[7].
- The antecedent dry period (i.e., with 0 – 0.05 inches of rain) no greater than two days will be preferred. A maximum antecedent dry period of 2 days is preferred to prevent input of excess suspended sediments in to the bioretention test columns.
- All key project personnel are reasonably anticipated to be present for the storm cycle.
- The storm takes place Monday, Tuesday, Wednesday or Thursday. This will allow time for the full set of tests for each storm to take place (Section 4.2.2).

The sampling site is situationally unique (Figure 1) and therefore lacks a specific sampling SOP to reference. Refer to the field sampling plan (FSP) (Appendix B) for detailed site-specific sampling procedures. In summary, at the sampling location, stormwater flows through a network of PVC pipes with various access ports. The stormwater samples for this study will be collected by manually opening a dedicated supply valve that feeds dedicated tubing.

Once flow is initiated though the tubing, stormwater containers will be filled. A grab sample will be collected and split in the field. At least 0.25 L will be placed in a labeled amber glass container and transported directly to KCEL where it will be analyzed immediately for 6PPD-Q or stored at ≤ 4°C until the remainder of water samples are analyzed. A second aliquot of the grab will undergo measurement of water quality characteristics at the time of sampling. The remainder of this grab will go to Bellingham and have measurements taken at various points and then travel back to KCEL to be analyzed for 6PPD-Q.

[7] The Project Team may sample storms with lower precipitation rates, including those as low as 0.15 inches in 12 hours. Such a change would be made if observations of the site support the assumption that flow would be adequate, and if project schedule requires sampling under conditions of lower rainfall rates.

Sample containers will be filled to maximum capacity and closures will be secured to minimize headspace, samples will be iced with wet ice and they will be covered to keep them dark during transportation.

Refer to the FSP (Appendix B) for the related safety plan, and Appendix D for an example of an FSU Field Sheet.

6.3 Containers, Preservation Methods, Holding Times

Table 10 summarizes the containers, preservation techniques, and holding times necessary to maintain water sample integrity following capture and during shipping to the laboratory.

Table 10. Sample Containers, Preservation, and Holding Times for Water

Parameter	Minimum Volume Required	Container	Preservative	Holding Time
Coho Acute Toxicity and bioretention influent (stormwater)	455 L	20-L Fluorinated FHDPE[b]	4°C (wet ice) in dark. Minimize head space.	Initiate test within 36 hours (refer to Section 3.5 on contingencies in the event coho have not sufficiently developed)
6PPD-quinone[a]	250 mL	250-mL amber glass	4°C (wet ice) in dark. Minimize head space, do not freeze.	4 weeks
Dissolved organic carbon (KCEL)	50 mL	125-mL amber glass	Filter through 0.45 µm filter then HCl to pH ≤ 2 within 1 day, ≤6°C	28 days
Dissolved organic carbon (Exact Scientific)	2 x 40 mL	Amber vial	Pre-preserved with phosphoric acid, no headspace	28 days
Total Suspended Solids (KCEL)	1 L	1-L WM HDPE	≤6°C	7 days
Total Suspended Solids Exact Scientific)	1 L	Plastic	None	7 days
Metals (Exact Scientific)	1 L	Plastic	Preserved with nitric acid at receipt	6 months

[a] – The volume shown includes water necessary for the matrix spike/matrix spike duplicate (MS/MSD).

[b] – This type of container and sample preservation will also be used to transport untreated stormwater following collection.

6.4 Field Challenges

Sampling will be performed during the late winter and early spring. Possible challenges for this study include:

- Navigating city streets during heavy rain events, especially while transporting large volumes of water.
- Maintaining small head spaces in all sampling containers, and keeping samples cool but not frozen. Freezing samples with small head spaces can break sample containers
- Maintaining an aggressive pace of a multifaceted project throughout each storm event.

To ensure samples are successfully transferred to the bioretention laboratory, properly collected and preserved sub-samples of stormwater from each storm will be shipped by KCEL to the laboratory immediately after collection. If a shipment is lost or damaged, including arriving at the laboratory in a compromised state, additional sampling will be conducted in subsequent storm events, either during later storms or at additional sampling locations. The basis for the sample handling and/or shipping problem that led to compromise of sample integrity will be defined and alternatives will be used or developed to prevent additional problems.

6.5 Equipment Decontamination

Field sampling equipment will be decontaminated prior to use. Sample containers will be provided by the analytical laboratories. Carboys will be cleaned at KCEL according to its internal protocols between storms.

6.6 Sample ID

Field sheets generated by KCEL's Laboratory Information Management System (LIMS) will be used at all stations and will include the following information:

1. Login number
2. Locator, unique to each sampling location
3. Date and time of sample collection
4. Initials of all sampling personnel
5. Water quality parameters (pH, temperature, DO, specific conductance & ORP)
6. Laboratory analyses required

LIMS-generated container labels will identify each container with a unique sample number, sampling location and description, container type, collection date, and analyses required.

In addition to LIMS numbers, descriptive sample identifiers (client locators) will be assigned to each sample. The client locator will consist of sequenced alphanumeric character codes as follows:

(storm event: timepoint)_(sample type)_(treatment type)_(treatment replicate)_(process point[8])

For example, an untreated sample collected from the second storm event would be identified as: S2T1_U_NT_NA

A treated effluent composite sample from the third storm event from high performance mix 1 would be identified as: S3T4_T_HP1_MX_EC

The Field Sheet (Appendix D) will also be used to record general weather and any deviations from the sampling plan, excessively warm ambient outdoor temperatures and unexpectedly high turbidity in the stormwater sample.

6.7 Chain of Custody

The data to be generated for this project are not for regulatory use. KCEL's field sheets will serve as chain-of-custody forms and will accompany samples being transported from each sampling location (i.e., the stormwater sampling location and the Bioretention Laboratory). Field sheets will be used to ensure the condition of samples (e.g., ice is still present) following each sample transportation step, timing of key handling steps, and the personnel involved.

Completed field sheets (example in Appendix D) will be included in coolers used to transport samples to KCEL, protected in a sealed Ziploc bag. FSU has responsibility for managing and completing field sheets up to the point that samples are delivered to KCEL. Upon receipt of all samples at KCEL following bioretention treatment, the Laboratory Project Manager will scan or photograph the completed field sheet and deliver it to the King County Project Manager who will file the completed field sheets in the appropriate project folder. The Laboratory Project Manager will file the original records.

6.8 Field Log Requirements

Sample records will be maintained on field sheets by King County staff and the Bioretention Laboratory Manager as part of participation in sampling or in collection of bioretention media column effluents. Sampling information and sample metadata will be documented using waterproof field notebooks; results of measurements for water quality characteristics will be recorded on the field sheet.

During sample collection, field notebooks will include the following information:

- Name of project and sampling location
- Field personnel performing sampling

[8] If applicable

- Field conditions and relevant notes on sample handling and transport
- Any changes or deviations from the QAPP or SOPs
- Environmental conditions
- Date, time, locator, pre-login number, and description of each sample
- Identity of QC samples collected
- Unusual circumstances that might affect interpretation of results.

7.0 LABORATORY PROCEDURES

Summaries of laboratory procedures for analysis of 6PPD-Q and the target analytes in flush water are provided below.

7.1 Analytical Lab Procedures

A summary of laboratory procedures and QA specifications for analysis of the 6PPD-Q and other targeted analytes is provided in Table 11.

DOC will be analyzed by KCEL SOP #3036 and SM 5310-B. DOC samples are first filtered through a 0.45µm filter. Addition of hydrochloric acid and sparging by the instrument removes inorganic and volatile carbon from the sample. The non-purgeable organic carbon (NPOC) remaining is converted to carbon dioxide by catalytic conversion in a heated combustion chamber packed with platinum catalyst. The carbon dioxide is measured directly by a non-dispersive infrared detector. The value provides a measure of non-purgeable organic carbon in the sample. In practice, the purgeable organic carbon is negligible, and therefore, the NPOC equals DOC on samples filtered through a 0.45µm filter.

TSS will be determined by KCEL SOP #3009 and SM 2540-D. For the determination of TSS, a measured volume of a well-mixed sample is filtered through a glass fiber filter. The residue retained on the glass fiber filter is dried to a constant weight at 103-105°C. The resulting net weight represents the total suspended solids.

6PPD-Q will be quantified by liquid chromatography/triple quadrupole mass spectrometry using an isotopically-labeled internal standard (D_5-6PPD-Q) method as in Hunt et al., (2021) as documented in KCEL SOP# 4077v0. The LCMS/MS system consists of an Agilent 1290 Infinity II LC system equipped with an Agilent Infinity Lab Poroshell 120 EC-C18 analytical column, coupled to an Agilent Technologies 6470 triple quadrupole mass spectrometer. A 6PPD-Q precursor ion and three of its products are monitored in positive MRM mode. The presence and ratio of these ions is used to confirm 6PPD-Q identification. Quantification is achieved using 6PPD-Q calibration standards spiked with an isotopically labeled internal standard, D_5-6PPD-Q.

7.1.1 Special Method Requirements

There are no special method requirements other than what is described in laboratory and field SOPs (Appendix C).

7.1.2 Laboratory Accredited for Methods

KCEL will perform laboratory-based chemical analyses for 6PPD-Q. KCEL does not hold accreditation for the 6PPD-Q test. KCEL has submitted an accreditation package to the Ecology Laboratory Accreditation Unit for the LC-MS/MS instrumentation to quantify 6PPD-Q in water samples. The accreditation package is currently under review.

Both Exact Scientific and KCEL are accredited by Ecology for analysis of metals and TSS; accreditation for the other analytes is not offered.

KCEL is accredited for acute fish toxicity testing by EPA Test Method 2019.0 and Method 2000.0.

Table 11. Surface Water Measurement Methods (Laboratory).

Analyte	Sample Matrix	Analytical (Instrumental) Method*
6PPD-quinone	Untreated stormwater Treated stormwater	KCEL SOP# 4077: 6PPD-quinone by LCMS/MS
Dissolved Organic Carbon	Untreated and treated stormwater used in toxicity tests	SM 5310-B
Total Suspended Solids	Untreated stormwater Treated stormwater	SM 2540-D
Metals	Flush water	EPA Method 200.8

7.2 Fish Acute Toxicity Test Laboratory Procedures

Toxicity tests will be performed according to EPA Test Method 2019.0: *Rainbow Trout,* Oncorhynchus mykiss*, and Brook Trout,* Salvelinus fontinalis*, Acute Toxicity Tests with Effluents and Receiving Waters* (modified by using coho as test organism); EPA Test Method 2000.0 *Fathead Minnow,* Pimephales promelas*, acute toxicity tests with effluents and receiving waters*; and USEPA (2002). Additional QA/QC guidance comes from Ecology's (2016) *Laboratory guidance and whole effluent toxicity test review criteria.*

Planned test conditions are summarized below (Table 12). Due to the nature of the project, compromises may need to be made on fish age, sample volumes and replication; any deviations from the QAPP will be noted in the data reports.

Table 12. Coho Acute Toxicity Test Summary

Condition	Specification
Organism	coho salmon (*Oncorhynchus kisutch*)
Test Type	Static non-renewal
Sample Hold Time	Initiate within 36 hours of sample collection
Temperature	12 ± 2°C
Dilution Water	Well Water hardness 80-100 mg/L as $CaCO_3$
Light Intensity	500-1000 lux
Photoperiod	16 h light:8 h dark
Test Chamber Size	2 gal. glass wide mouth jar or 18L glass jars
Renewal of Test Solution	None
Age of test Organisms	Should be 15 to 30 days
Test Concentrations	100% sample
Number of Organisms	10
Number of Replicates	4
Feeding	None during test and ceased 48 hrs. prior to test initiation
Oxygen/Aeration	None, unless DO concentration falls below 6.0 mg/L
Positive Control	6PPD-Q (one LC_{50} test per batch of test organisms)
Test Duration	24 hours
Endpoint	Mortality and observational notes of suspected URMS symptoms (disorientation, swimming in circles, gaping, etc.) will be made in the first 12 hours of exposure.
Test Acceptability	≥90% control survival
Measurements	Temperature, pH, dissolved oxygen (daily for each)
Water Quality	Hardness, Alkalinity, Conductivity, redox (0-hour for each)

7.3 Measurement of Water Quality Characteristics

The water quality characteristics (pH, specific conductance, oxidation-reduction potential, temperature and DO) will be measured in samples throughout each storm cycle (Table 2). Table 13 summarizes the methods for these measurements.

Table 13. Water Measurement Procedures (Field) in Stormwater and Bioretention media column Effluents

Analyte	Expected Range of Results	Sample Prep Method	Instrument
pH	4 - 10	There is no sample preparation required. These measurements will be taken in a discrete aliquot using a separate, wide mouth container and will be disposed following measurements.	YSI EXO Multiprobe
Specific Conductance	20 – 500 mS/cm		YSI EXO Multiprobe
Oxidation Reduction Potential	-150 to +150 mV		Hanna ORP Meter
Dissolved Oxygen	2 – 14 mg/L		YSI EXO Multiprobe
Temperature	10 – 19 °C		YSI EXO Multiprobe

8.0 QUALITY CONTROL PROCEDURES

Quality control for King County water quality monitoring programs is maintained by use of trained and experienced personnel in all aspects of its programs. King County and the Bioretention Laboratory will collaborate on QA/QC procedures for the purposes of this project. King County and the Bioretention Laboratory rely on the professionalism and care of each other's personnel in maintaining sample integrity when samples are being collected and in the custody of field personnel.

8.1 Field and Laboratory Quality Control

The analytical QA regime is summarized in Table 8, and field measurement specifications are in Table 9. This project will not include field duplicates because of the complexity of the process that each sample undergoes. Quality control will result from staff adherence to protocols, as described previously. Assignment of data qualifiers is described briefly below.

8.1.1 Analytical Chemistry

Asterisks are automatically applied by LIMS to QC data on the QC report to identify situations where results may be outside defined acceptance criteria. This step is done by the QC CALC process that is included in LIMS process chains. For example, "*" is applied if the RPD of the LD is outside the acceptance limit specified in the method. Data flags are then applied, if necessary, as outlined in KCEL's QA Manual, Appendix C.

Samples with 6PPD-Q concentration below the MDL are reported as a null value with a <MDL qualifier. Samples with results between the MDL and the Reporting Detection Limit (RDL) are reported as a numeric value and a <RDL qualifier.

8.1.2 SPLP

The laboratory to perform SPLP has not yet been selected. The selected laboratory will be required to apply EPA Method 1312, consistent with Ecology (2021). Leachates will be analyzed for nitrate + nitrite, TP, OP and total copper with EPA Methods 353.2, SM 4500-P-E-95, and 200.8 respectively. Laboratory qualifiers will be defined in laboratory reports.

8.1.3 Toxicity Testing

QA/QC guidance for the acute toxicity tests comes from Washington State DOE, 2018. *Laboratory guidance and whole effluent toxicity test review criteria.* DOE publication #WQ-R-95-80.

8.1.4 Bioretention Laboratory Preparation

Section 3.1 describes preparation of the Bioretention Laboratory, the quality of materials to be used, and generation of information to facilitate accurate data interpretation by addressing these confounding factors: a) introduction of toxicants to effluent water by

bioretention media and b) addressing loss of 6PPD-Q to the bioretention equipment, which will directly affect interpretation of bioretention effectiveness.

8.2 Corrective Action Processes

Project personnel will review field and sample documentation (field sheets, laboratory reports) to ensure that processes were performed according the QAPP specifications, and to check for deficiencies and nonconformances. Deficiencies are unauthorized deviations from procedures documented in the QAPP. Nonconformances are deficiencies that affect quality and render the data unacceptable or indeterminate, such as:

- Deficiencies
  - COC deviations, such as incorrect time of sample collection or measurement
  - Exceedances of holding time requirements
- Nonconformance
  - Using the wrong sample containers
  - Failure to calibrate instruments according to appropriate protocols.

Deficiencies or nonconformances are reported to the King County Project Manager and Laboratory managers, and corrective actions are applied (when possible) in a timely manner. The Laboratory Managers are responsible for implementing and tracking corrective action procedures based on findings of periodic reviews. Records of corrective actions are maintained by the King County Project Manager. Field deficiencies and nonconformances are documented by FSU in field notebooks and may be noted in reports.

The King County Project Manager will work closely with KCEL and the Bioretention Laboratory conducting the data review to examine data that fall outside of QC criteria. The Project Team will collaborate to determine whether data should be re-analyzed, rejected, or used with appropriate qualification.

9.0 DATA MANAGEMENT PROCEDURES

Data for this project will be generated by KCEL's FSU (sampling location coordinates and of water quality measurement) and by three separate analytical laboratories:

- Bioretention media and materials testing using SPLP; nitrogen, phosphorus and copper in leachates (laboratory to be determined).
- Metals, TSS and DOC in flush water (Exact Scientific)
- 6PPD-Q in flush water at the end of the flushing process (KCEL)
- 6PPD-Q, TSS, DOC in untreated stormwater, influents, and effluents (KCEL)
- Fathead minnow toxicity test of final flush water and coho toxicity tests (KCEL)

Data management procedures for each are outlined below.

9.1 Data Recording and Reporting Requirements

Information from sampling events and measurement of the water quality characteristics will be recorded in field logbooks or on field sheets (see example in Appendix D) at the time of collection (Table 2). Data collected on field sheets will uploaded to LIMS by King County staff following completion of each field sampling event.

Laboratory data will be recorded by Exact Scientific, KCEL and the SPLP and Bioretention laboratories according to their internal data handling protocols.

9.2 Laboratory Data Package Requirements

KCEL, the SPLP laboratory and Exact Scientific will provide findings to the King County Project Manager in electronic form when the work has been completed. This will include detailed results presented in a standard Level 2 data package (Excel spreadsheets) that includes a general narrative and reports on the analysis of the contracted chemicals. The laboratories will provide all relevant QC data as well, such as reports on matrix spike analyses, precision and recovery.

10.0 AUDITS AND REPORTS

There are no audits planned for this project, but audits may be performed by Ecology at its discretion.

10.1 Audits

Project laboratories participate in performance and system audits of their routine procedures. No audits are planned specifically for this project.

10.2 Frequency and Distribution of Reports

The King County Science section will prepare a Project Report for submittal to Ecology on or before June 30, 2023, at which time, all laboratory tasks are expected to be complete. The Project Report will summarize methods, procedures as performed, and will include each laboratory's report with QA/QC relevant to each laboratory's actions, and the Field Procedures Report prepared by FSU.

The Project Team will prepare an interpretive report that summarizes the methods, results, and lessons learned. The interpretive report will be complete in the fall of 2023.

11.0 DATA VERIFICATION

Data verification is the process of evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual requirements (EPA, 2002).

11.1 Field Data Verification

Field data for this project are limited. Location of sampling (i.e., sampling coordinates) will be verified by the Field Lead or designee using information from this QAPP. Quality of data for water quality characteristics will be ensured by close adherence to the instrument calibration procedures, and documentation of calibration events.

11.2 Laboratory Data Validation and Verification

For all targeted chemical analytes, King County will perform Stage 2A laboratory data validation and verification (USEPA, 2009), including:

- Check of the analytical data package for completeness and verification that all data requested are present in the data deliverables.
- Review all analytical QA/QC data for acceptance using the DQOs defined in this QAPP.
- Laboratory compliance with QAPP requirements for conditions of samples upon receipt, and the comparison of QC results in the analytical data package to specified acceptance criteria, guidelines, and requirements according to the analytical methods. Attainment of both sample-related and instrument-related quality criteria will be verified.

King County will not use a third party to perform data validation. Reporting and documentation of this review are described in Section 12.

12.0 DATA QUALITY AND USABILITY ASSESSMENT

The King County Project Manager or designee will assemble a data quality assessment report following completion of all experimental steps. The report will summarize results of data quality controls, identify when data quality objectives were not met, and discuss resulting limitations (if any) on the use or interpretation of the data. Rejection of analytical data is not anticipated. The assessment of data usability will be documented in an appendix of the final report.

12.1 Process for Determining Project Objectives Were Met

Project outcomes will be considered to have met the original objectives if the field and analytical data are generated according to the specifications of this QAPP and consistent with the study design, methods, and procedures described herein. The King County Project Manager will provide or assign an independent review of the water quality QC data from each storm cycle using the MQOs that have been identified in this QAPP. The Project Team will present results of the QA process in a data validation report; this will be attached to the final documentation for this project.

Specific QA information that will be noted in the data quality assessment report includes the following:

- Changes in and deviations from the QAPP
- Results of performance or system audits
- Significant QA problems
- Data quality assessment results in terms of precision, bias, representativeness, completeness, comparability, and reporting limits.
- Discussion of whether the QA objectives were met, and the resulting impact on decision-making.
- Limitations on use of the measurement data.

12.2 Treatment of Non-Detects

Censored analytical results (i.e., non-detects) for any chemistry concentration including 6PPD-Q indicate that the chemical is at a concentration below the qualitative and quantitative limits of detection or absent. Censored results will be used to establish study designs for future studies by indicating a need for a lower reporting limit.

12.3 Data Analysis and Presentation Methods

Data analysis will be conducted to document the performance of the BSM blends for pollutant removal effectiveness and relative to treatment goals, as specified in the DQOs

(Appendix A). The DQO summaries provide a taking off-point for data analysis and exploration, they are not intended to describe limits to the analysis approach.

12.4 Data Analysis Approach

Statistical comparisons and graphical presentations of resulting data as described in the DQOs (Appendix A) will be conducted in R, Excel or other analytical or graphics format. Presentation of results will include summary tables of 6PPD-Q analytical and toxicity test results; and graphical representations showing the performance of each bioretention treatment type in 6PPD-Q removal and toxicity reduction efficiency. We expect to perform various comparisons among treatment types, storms and with the literature. Covariation between water quality characteristics and 6PPD-Q concentrations over time or with toxicity outcome will be evaluated and presented as appropriate. Uncertainties will be described and addressed.

12.5 Evaluation of Treatment Performance

To evaluate the treatment performance of the various BSM blends, both statistical and qualitative comparisons will be performed for each parameter from each flushing and dosing event.

We will compare influent and effluent concentrations of 6PPD-Q, TSS, and DOC to evaluate the effect of each bioretention type on each of these factors. Comparisons will address whether there are differences in 6PPD-Q concentrations between the influent and effluent of each BSM blend across individual sampling events, and whether those differences change over the course of the project.

The specific null hypothesis (H_o) and alternative hypothesis (H_a) for these analyses are as follows:

> *H_o: Effluent pollutant concentrations are not different than influent concentrations.*
> *H_a: Effluent concentrations are less than influent concentrations*.

Results of these comparisons and changes in performance over time will inform a ranking of the tested BSM in terms of pollutant removal efficiency.

We will also evaluate measurements of water quality characteristics in a similar way, though we do not have specific expectations that any of them will be lower in effluent than in influent. The analysis will evaluate whether there is correspondence between concentrations of 6PPD-Q and one or more of the water quality characteristics, TSS or DOC.

12.6 Sampling Design Evaluation

Field sampling for this project is relatively simple, and we do not anticipate a complex retrospective evaluation.

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Appendix A: DQO Summaries

DQO Steps	DQO 1: 6PPD-Q removal or reduction effectiveness
Step 1. State the Problem	**PROBLEM:** Untreated stormwater from some locations in King County contains 6PPD-Q, a toxic chemical that causes acute mortality in coho salmon, a.k.a."urban runoff mortality syndrome" (URMS). Bioretention using a high-compost bioretention soil media (BSM; 60% sand/40% compost blend) has been shown in bench-scale lab studies to eliminate coho toxicity. However, this BSM leaches phosphorus, copper and potentially other stormwater constituents into treated effluent. King County requires information on the effectiveness of different configurations of the high-performance BSM (HPBSMx) in reducing concentrations of 6PPD-Q in stormwater, thereby reducing risk of URMS in freshwaters within King County. The HPBSM of interest is one approved for use in bioretention systems by Ecology. There are three configurations of Ecology-approved HPBSM, consisting of a three-part primary layer (Type 1); or Type 1 with a polishing layer (Type 2); or Type 1 with a polishing layer and a 2" compost surface layer (Type 3). The problem to be addressed by this study is whether the new Ecology-approved HPBSMx can reduce the concentration of 6PPD-Q in stormwater ([6PPD-Q]) to below levels toxic to coho (i.e., the estimated LC_{20} of 0.060 µg/L), and whether they perform better or worse at this function than traditional BSM. **PLANNING TEAM**: King County Department of Natural Resources and Parks (DNRP), Water and Land Resources Division (WLRD): Toxicology and Contaminant Assessment (TCA) Unit of the Science and Technical Services (STS) Section;, Stormwater Services Section (SWS); and King County Environmental Laboratory (KCEL), including the Field Sciences Unit (FSU); and Curtis Hinman and Associates. **DECISION TEAM**: Project Manager (Jenée Colton) will advise leadership of SWS, WLRD, and DNRP of results; WLRD and DNRP leaders will apply results to County actions. **RESOURCES AND DEADLINES**: Financial: STS Operating funds; Ecology grant Facilities: Bioretention Laboratory (column setup and testing); KCEL (sampling equipment, analytical chemistry, toxicology). Deadlines: Project completion by June 30, 2023. Storm events in February, March, and April 2023, as needed. Laboratory Preparation: Bioretention test columns to be ready in February 2023. KCEL ability to analyze effluent toxicity to be ready in early February 2023.
Step 2. Identify the Goal of the Study	**DECISION TO BE RESOLVED**: Whether the Ecology-approved HPBSM effectively treats stormwater at the bench scale to remove/reduce 6PPD-Q. Whether any of the HPBSMx perform as well or better at this than traditional BSM (60/40 mix). **STUDY QUESTIONS** 1. Is [6PPD-Q] in untreated stormwater influent ≥ [6PPD-Q] in treated effluent for 60/40 BSM and HPBSMx? 2. Which BSM or HPBSMx generates the greatest reduction in [6PPD-Q]? 3. Does treatment of stormwater with BSM or HPBSMx generate effluent with [6PPD-Q] ≤ 0.060 µg/L? Does treatment of stormwater with BSM or HPBSMx generate effluent with [6PPD-Q] < the method detection limit (MDL)? 4. Is the overall performance of the HPBSMx in removing 6PPD-Q as good or better than that of 60/40 BSM?

	ACTONS/OUTCOMES: There is a wide range of possible study outcomes, including that one or more HPBSMx does not reduce 6PPD-Q; or that [6PPD-Q] is lower in effluents than in influents but is still potentially toxic. Expected action: a technical recommendation to SWS regarding the effectiveness of BSM and one or more HPBSMx for addressing URMS. The recommendation will include any caveats or uncertainties that arise due to unexpected outcomes, including recommendation for further study. **Alternative Outcomes**: 1. [6PPD-Q] is not sufficiently reduced in HPBMx-treated stormwater to be below toxic concentrations (LC_{20}). 2. [6PPD-Q] is below the LC_{20} or below the MDL in treated stormwater, but treated stormwater is toxic to coho. Additional testing of the HPBSMx in a future study would evaluate causes of mortality other than 6PPD-Q; or future studies of toxicity of stormwater could evaluate covariates with toxic potency of 6PPD-Q.
Step 3. Identify Information Inputs	**To resolve the decision identified in Step 2, the following information will be needed**: <u>Study Questions 1, 2 and 4</u> 1. [6PPD-Q] in representative samples of untreated stormwater just prior to treatment, and after treatment for BSM and each HPBSMx; replicated for three separate storm events. 2. [6PPD-Q] in treated stormwater effluent from BSM and each HPBSMx, replicated for three separate storm events. <u>Study Question 3</u> 1. [6PPD-Q] in representative samples of untreated stormwater a) at the time of collection, and b) at the time treated stormwater is analyzed and c) toxicity tests are performed (later in the process). <u>All Study Questions</u>: Consistency in performance of BSM and each HPBSMx in reducing [6PPD-Q] in treated stormwater over the course of three storms. Results of the study under DQO2- Stormwater Toxicity. Documentation of adherence to study protocols regarding sample handling, stormwater treatments, measurement of ancillary variables, and toxicity tests.

Step 4. Define the boundaries of the Study	**Temporal Boundaries**: Stormwater samples will be collected in February, March and possibly April of 2023. Each trial will be followed by at least one week prior to additional testing, depending on the needs of the laboratories to prepare and perform the work. Schedule guidelines: a. Each treatment trial is expected to be complete within 72 hours of the sample receipt by the HPBSM column testing laboratory. b. Transport of treated effluents in sample containers to KCEL will be complete within 6 hours of completion of treatment trials. c. Each analysis of 6PPD-Q is expected to complete within a few days of receipt of samples by KCEL (and in accordance with holding times specified in this QAPP). d. Transport of untreated stormwater to KCEL immediately upon collection for analysis of [6PPD-Q]. Tests of chemistry and toxicity for all three storms to be completed by May 31, 2022. These are guidelines, actual hold times and project schedule details are as described in the QAPP. **Spatial Boundaries**: A single source of stormwater will be used for all three tests. **Practical constraints on data collection:** Instability of 6PPD-Q may cause changes in concentration between sample collection and testing, between different parts of the column setup, etc., that could confound results. The sampling, bioretention treatments, and chemical and toxicological testing will take place in a very short time frame, with samples maintained at ≤ 4°C, and protected from light exposure.
Step 5. Define the Analytic Approach	**Decision rule (if/then statement)**: If the mean [6PPD-Q] in treated effluent from any HPBSMx consistently less than the mean [6PPD-Q] in untreated influent and less than [6PPD-Q] in untreated stormwater of same age; or the [6PPD-Q] is reduced from above to below the coho LC_{20} (0.060 µg/L) consistently by the HPBSMx, then the HPBSMx will be considered a potentially effective treatment for reduction or elimination of 6PPD-Q in stormwater of comparable source and make-up of the stormwater samples tested in this experiment. If under these conditions, the [6PPD-Q] in treated effluent is < MDL, the treatment type will be highly recommended. **Data analytical approach**: 1. One-way statistical comparison of [6PPD-Q] in untreated stormwater influent with that of a) treated effluent for BSM and each HPBSMx, and b) untreated stormwater of the same age, using a statistical tool appropriate to the data (e.g., Kruskal-Wallis; MannWhitneyWilcoxan) 2. Qualitative evaluation of results for a) net reduction in mean influent and effluent [6PPD-Q] and b) consistency with results of toxicity tests and evaluation of potential water quality controls on [6PPD-Q] and bioavailability (DQO 2). 3. Direct comparison of the upper 95% confidence interval on the mean [6PPD-Q] in treated effluent by storm, and by HPBSMx, to LC_{20} for coho and to the 6PPD-Q MDL.
Step 6. Specify Performance or Acceptance Criteria	**Statistical Design**: Untreated stormwater over time: a) at the time of sampling, b) at the time of the toxicity tests at KCEL. Stormwater influent for [6PPD-Q] N = 3 Treatment BSM and HPBSMx Effluent: N = 3 of each treatment. N = 4 treatments (BSM, Type 1, Type 2 and Type 3 HPBSM)

	N = 3 storms (i.e., independent stormwater samples) 1. These sample numbers assume [6PPD-Q] variance for receiving water from Johannesen (2021) and KCEL (2022) for method development reflect KCEL's analytical variance for stormwater influent and effluent, respectively. 2. Estimate difference in influent and effluent [6PPD-Q] by subtracting the mean concentration in effluent by treatment from the mean in influent. **Range of parameter of interest**: -We expect untreated stormwater from an interstate freeway to contain [6PPD-Q] as documented previously: 0.8 - 19 µg/L (Tian et al., 2021, with high-bias). On the basis of samples collected by KCEL in 2022 and 2023, [6PPD-Q] in the stormwater source is expected to be 0.5-2.0 µg/L. - [6PPD-Q] in stormwater-affected water bodies could be 2.30 ±0.05 µg/L (Johannessen et al. 2021). -We expect the LC_{20} for coho salmon to be 0.060 µg/L (Tian et al., 2022); though this value may be affected by constituents of stormwater (Tian et al., 2021). -We expect low analytical variation of 6PPD-Q in controlled laboratory settings based on trials in method development (KCEL, 2022); std dev = 6-8% of arithmetic mean. **Null hypotheses**: [6PPD-Q] in stormwater influent < [6PPD-Q] in treated effluent for HPBSMx. [6PPD-Q] in treated stormwater effluent ≤ LC_{20} for coho for HPBSMx. [6PPD-Q] in treated stormwater effluent ≤ MDL for HPBSMx. [6PPD-Q] in stormwater influent when sampled = [6PPD-Q] in untreated stormwater at the time of toxicity testing of effluents. **Decision Errors** Study Questions 1, 3**:** Probability of Type I error: $\alpha \leq 0.10$. Probability of Type II error: β (statistical power = 1 - $\beta = 0.80$). Study Questions 2, 4: Qualitative comparisons will be performed. Comparison of the 95% UCL on the mean effluent [6PPD-Q] per HPBSMx in comparison to coho LC_{20}; this approach allows only 5% chance of incorrectly concluding that the HPBSMx is effective.
Step 7. Develop the Plan for Obtaining Data	The QAPP provides the plan for collecting data.

DQO Steps	DQO 2: Stormwater toxicity removal or reduction effectiveness
Step 1. State the Problem	**PROBLEM:** In consideration of the Problem Statement in DQO 1, King County requires information to evaluate specific Ecology-approved BSM and HPBSM configurations (HPBSMx) for stormwater treatment effectiveness for water quality to eliminate lethal toxicity to coho salmon. **PLANNING TEAM**: King County Department of Natural Resources and Parks (DNRP), Water and Land Resources Division (WLRD): Toxicology and Contaminant Assessment (TC) Unit of the Science and Technical Services (STS) Section; Stormwater Services Section (SWS); and King County Environmental Laboratory (KCEL), including the Field Sciences Unit (FSU); with Curtis Hinman and Associates. **DECISION TEAM**: Project Manager (Jenée Colton) will advise leadership of SWS, WLRD, and DNRP of results; WLRD and DNRP leaders will apply results to County actions. **RESOURCES AND DEADLINES**: Financial: STS Operating funds; Ecology grant Facilities: Bioretention Laboratory (column setup and testing); FSU (sampling equipment); KCEL (analytical chemistry, toxicology). Deadlines: Project completion by June 30, 2023. Storm events in February, March and April 2023, as needed. Laboratory Preparation: Bioretention test columns to be ready in February 2023. KCEL ability to analyze effluent toxicity to be ready in February 2023.
Step 2. Identify the Goal of the Study	**DECISION TO BE RESOLVED**: Whether any of the HPBSMx tested effectively treat stormwater to remove/reduce or eliminate stormwater toxicity to coho relative to untreated stormwater at the bench scale. Whether any of the HPBSMx perform as well or better at this than traditional BSM (60/40 mix). Which treatment type can be recommended to SWS for use in addressing URMS. **STUDY QUESTIONS** 1. Is treated stormwater effluent from 60/40 BSM and HPBSMx Types 1 and 3 toxic to coho? 2. Is untreated stormwater influent more or less toxic to coho than treated stormwater effluents? 3. What is the [6PPD-Q] in toxic stormwater and in non-toxic stormwater? (see DQO1) 4. Do common constituents of treated stormwater effluent (dissolved organic carbon and total suspended solids; DOC and TSS) covary with toxicity to coho? **ACTONS/OUTCOMES**: 1. One or both Type 1 and Type 3 HPBSMx consistently reduce or eliminate toxicity to coho in treated stormwater effluent relative to untreated stormwater. 2. Reduced toxicity is consistent with reduced [6PPDQ]. 3. Toxicity can be explained by [6PPDQ] and/or other water quality variables in toxicity test water that may affect 6PPDQ degradation rate or bioavailability. 4. Type 1 and Type 3 HPBSMx are as effective or more effective than BSM at reducing or eliminating toxicity of stormwater to coho. **Alternative Outcomes**: 1. Treated stormwater is toxic to coho in some or all of the trials. 2. Treated stormwater is toxic to coho inconsistently or inconsistent with expectations based on [6PPDQ]. 3. Ancillary water quality variables (TSS and DOC) in toxicity test water are irrelevant or not clearly relevant to understanding the toxicity of the effluents. 4. HPBSMx performs poorly relative to BSM in reducing or eliminating toxicity.

Step 3. Identify Information Inputs	**"Coho Toxicity"** is measured as the number of dead fish per chamber (with 5 fish exposed in each chamber), with four test chambers per effluent composite. The result will be recorded as (X/5) fish dead within 24 hours. To resolve the decision identified in Step 2, the following information will be needed: <u>Study Questions 1, 2 and 3.</u> 1. Coho toxicity of representative samples of treated and untreated stormwater All information listed above replicated for three separate storm events. <u>Study Question 3</u> 1. Results for DQO 1. <u>Study Question 4</u> 1. Results of both toxicity test for treated and untreated stormwater, and results for TSS and DOC in the effluent composites used in toxicity tests.
Step 4. Define the boundaries of the Study	**Temporal Boundaries**: Same as for DQO 1. Tests of chemistry and toxicity for all three storms to be completed by May 31, 2023. **Spatial Boundaries**: A single source of stormwater will be used for all three tests. **Practical constraints on data collection:** See practical constraints for DQO 1.
Step 5. Define the Analytic Approach	**Decision rule (if/than statement)**: If the toxicity of treated effluent from any BSM or HPBSMx (in terms of average mortality of each treatment type) is consistently less than in untreated stormwater of same age; or the toxicity is present in untreated stormwater collected at the same time as treated stormwater, but absent in the treated stormwater effluent, then the BSM or HPBSMx will be considered a potentially effective treatment for reduction or elimination of coho toxicity in stormwater of comparable source and make-up of the stormwater samples tested in this experiment. "Consistently" in this decision rule means 2/3 or greater of all effluent toxicity tests. **Data analytical approach**: 1. Qualitative evaluation of results for: a). Difference in mortality of influent and effluent b). Consistency with results of [6PPDQ] measurements (DQO1) and evaluation of potential water quality controls on 6PPDQ bioavailability (TSS and DOC) c). Consistency in toxicity test results between storm events (as defined above), for any given treatment type.

Step 6. Specify Performance or Acceptance Criteria	**Statistical Design**: Untreated stormwater influent for toxicity N = 1 Treatment BSM and HPBSMx effluent = 1 composite of 3 effluents N = 3 treatments (effluents of Type 2 HPBSM will not undergo toxicity tests) N = 3 storms (i.e., independent stormwater samples) This regime is repeated for each of three storms **Range of parameter of interest**: Average mortality after 24 hours exposure (mean of 5 fish exposed) in 4 replicates: 0 – 5. Lethality present/absent **Null hypotheses**: Effluent of HPBSMx is not toxic to coho Effluent of HPBSMx is less toxic to coho than untreated stormwater influent Effluent of HPBSMx is as toxic to coho than effluent of 60/40 BSM Concentrations of TSS and/or DOC in toxicity test water covary with fish mortality. **Decision Errors** There is no quantitative decision error statement for this DQO. <u>All Study Questions</u> Qualitative comparisons will be performed by comparing fish mortality: - Between BSM and HPBSMx treatments, per treatment, per storm; and overall (all storms combined). - Between BSM and HPBSMx treatments and untreated stormwater of the same age. Consistency of BSM and HPBSMx treatment effectiveness for toxicity will be evaluated. If HPBSMx effluent is toxic in > 2 of 3 storms, the HPBSMx will not be considered potentially effective in reducing coho toxicity. Additional studies to address potential causes of the toxicity other than 6PPDQ would be recommended.
Step 7. Develop the Plan for Obtaining Data	The QAPP provides the plan for collecting data.

Appendix B: Field Sampling Plan

King County

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TECHNICAL MEMORANDUM

Date February 28, 2023

TO: Jenée Colton, Water Quality Planner, WLRD, DNRP
Curtis Hinman, Curtis Hinman and Associates
Fran Sweeney, Aquatic Toxicology Unit Supervisor, KCEL, WLRD, DNRP

FM: Christopher Barnes, Environmental Lab Scientist, WLRD, DNRP
Jennifer White, Water Quality Planner, WLDR, DNRP

RE: Field Sampling Plan: Bioretention Media Blends Effectiveness, 6PPD-Q

This memorandum provides sampling details to personnel participating in a study involving collection and transport of stormwater runoff from I-5 to be accessed from a defined location (Figure 1). Field work includes sample collection and management, collection and management of samples during laboratory procedures, and measurement of specific water quality characteristics with a multiparameter water quality sonde and an oxidation-reduction potential (ORP) meter at defined time points.

The project is detailed in the *Testing Removal of 6PPD-Q and Coho Salmon Lethality by High Performance Bioretention Media Blends, Quality Assurance Project Plan* (QAPP). Users of this memorandum should review the QAPP for more detailed information on the study.

Study Overview

Study Goals: King County seeks information on the effectiveness of Ecology-approved configurations of the high performance bioretention soil media (HPBSMx) and traditional 60% sand/40% compost (60/40) BSM in reducing concentrations of 6PPD-Q in stormwater (Ecology 2021), and/or reducing risk of coho salmon urban runoff mortality syndrome (URMS) in freshwaters within King County. This study consists of bench-scale soil column tests of three HPBSM types and the 60/40 BSM for effectiveness in reducing concentrations of 6PPD-Q and/or coho toxicity from field-collected stormwater. All samples for the bioretention column tests will be collected from the same location (Figure 1) using the facilities set up for the purpose of stormwater sampling (Figure 2). Collection and transport of the stormwater prior to and following the soil column tests is the subject of this plan.

Study goals are as follows:

- Generate information on whether 60/40 BSM or any of the HPBSMx can reduce the concentration of 6PPD-Q in stormwater ([6PPD-Q]) to below levels toxic to coho; and determine relative performance of each BSM at these functions.
- Measure stormwater quality variables throughout the process to evaluate whether these correlate with [6PPD-Q]. Results will describe how stormwater treatment affects each of these parameters relative to the natural aging of an untreated stormwater sample across the time frame of the study.

Roles and Responsibilities: Personnel involved in field sampling and sample processing include staff of King County Environmental Lab (KCEL) and the Field Science Unit (FSU). Project personnel names, contact information and roles and responsibilities are in Table 1. In general, King County FSU staff are responsible for collection and transport of samples (Table 2), and for measurement of water quality parameters at each time point designated in the QAPP. Activities of field personnel will include sample collection, storage and transportation of the untreated stormwater to the Bioretention Laboratory in Bellingham for treatment in bioretention soil columns; and collection, handling and transport of samples of treated effluents back to KCEL for toxicity tests and chemical analyses, as prescribed by the QAPP. Field staff will perform these actions according to sample container, handling and storage requirements (Table 3).

Table 1 Project Team Roles and Responsibilities

Staff	Title	Role/Responsibilities
Jenée Colton	Project Manager	Decisions on any deviations from the QAPP. Coordinates with Curtis Hinman and Associates. Contact in the event of an emergency involving King County personnel
King County, DNRP/WLRD		
Email: Jenee.Colton@kingcounty.gov		
CELL PHONE: 206-348-3861		
Phone LAND LINE: 206-477-4075		
Curtis Hinman	Bioretention Laboratory Manager	Decisions on any deviations from the QAPP. Contributes to the go/no-go decision on any given storm event.
Curtis Hinman and Associates		
Bellingham, WA 98225		
CELL PHONE: 253-330-9878		
Susannah Rowles	KC Laboratory Project Manager	Pre-log samples, prepare and set up bottle kits Contributes to the go/no-go decision on any given storm event. Coordinates with FSU and chemistry and toxicology laboratory units.
King County, DNRP, King County Environmental Laboratory (KCEL)		
Email: Susannah.Rowles@kingcounty.gov		
CELL PHONE: 206-510-6128		
PHONE LAND LINE: 206-477-7158		

Staff	Title	Role/Responsibilities
Christopher Barnes	King County Field Lead	Lead for KCEL FSU field sampling teams. Decisions on FSU field activities including any deviations from the QAPP. Tracks weather, communicates with project team, and makes go/no-go decision on any given storm event. Delegates responsibilities to other field team participants. Ensuring all FSU participants are familiar with all field procedures and have all necessary equipment and training. Personal health and safety while in the field. King County's central contact for field sampling efforts.
King County, DNRP, King County Environmental Laboratory (KCEL)		
Email: Christopher.Barnes@kingcounty.gov		
CELL PHONE: 206-445-5505		
PHONE LAND LINE: 206-477-7143		

The Field Lead is responsible for tracking the weather, identifying storms eligible for sampling according to project criteria, and notifying project team members during the storm tracking process. Communications that lead to a sampling event may occur on weekends if Monday sampling is required.

Sampling Approach

Stormwater Sample Collection Overview: Sampling will take place during three rainstorm events, likely within the first four months of 2023.

Field sampling will be conducted at one sampling location (Figure 1). Sample location GPS coordinates are: 47°39'22.6"N 122°19'19.8"W. Stormwater collection will be performed using available facilities at that location. A detailed schematic of the sampling location is in Figure 2.

The sampling process will consist of the following general steps, in the order that they will be executed, for each storm:

- Collect 455 L of stormwater from the sampling location (Figure 1) into 20 L fluorinated high density polyethylene carboys and store on ice, covered with a black tarp for transport to the Bioretention Laboratory
- Collect a grab sample of stormwater of about 2 L from the source in a fluorinated high density polyethylene bottle. From this grab, a subsample will be placed in a 250 mL amber glass bottle (Table 2) for immediate transport to KCEL for analysis or storage. In an additional 300 to 500 mL aliquot of this grab sample, measure and record information on water quality parameters (oxidation reduction potential [ORP], pH, dissolved oxygen [DO], temperature and specific conductance [SC]), and discard. The remaining volume of this 2 L grab will be transported to the Bioretention Laboratory for further measurements.
- Transport stormwater sample in 23 sample containers (20-L carboys) to the Bioretention Laboratory, where final compositing will take place.

- Perform water quality measurements and effluent water sampling at the Bioretention Laboratory; manage and store samples according to QAPP specifications.
- Transport samples to KCEL in Seattle.
- Log in all samples at KCEL, measure water quality conditions in the 4 composited effluent samples, untreated stormwater influent sample and untreated grab sample.
- Splits of composites for TSS, DOC, 6PPD-Q and water quality measurements will be conducted by the toxicology laboratory on the second day of the storm cycle.
- Store all samples at ≤ 4°C overnight at the KCEL facility.

All of these steps will be completed on Day 1; login of samples may occur on Day 2.

Decision to Sample: Weather forecasts will be monitored by the Field Lead or designee to identify potential storm events to be sampled; the Field Lead is responsible for communicating storm forecast and anticipated sampling to the team (Table 1). Target storm events will be those forecasted to result in at least 0.25 inch of rain in a 6-hour period. To prepare for sampling, the Field Lead will begin communication about any potential storm targeted for stormwater sampling approximately a week in advance.

The following are the criteria to be met for a storm to be considered for sampling:

- Target storm events will be those forecasted to result in at least 0.25 inch of rain in a 12-hour period[1].
- An antecedent dry period (0 to 0.05 inches of rainfall) no greater than two days will be preferred.
- All key project personnel[2] are reasonably anticipated to be present for the storm cycle. The storm takes place Monday, Tuesday, Wednesday or Thursday.

The Field Lead will consult with the Project Manager and Laboratory Project Manager during the process of making a decision about initiating a storm sampling event.

Sample Collection Equipment. Table 2 (which references Table 10 of the QAPP), provides a summary of sample container requirements, volumes, and storage and handling requirements, and sample collection and preservation for each sample type. Table 1 indicates that the KC Laboratory Project Manager has responsibility for provision of sample bottles.

[1] The Project Team may sample storms with lower precipitation rates, including those as low as 0.15 inches in 12 hours. Such a change would be made if observations of the site support the assumption that flow would be adequate, and if project schedule requires sampling under conditions of lower rainfall rates.

[2] Key personnel are Elizabeth Frame (6PPDQ analysis), the FSU Field Lead (Table1) or designee, and Curtis Hinman (Bioretention Laboratory, Table 1).

Table 2. Sample Volumes, Containers, Preservation and Holding Times

Parameter	Minimum Volume Required	Container	Preservative	Holding Time
Stormwater (untreated)	455 L	20L Fluorinated HDPE	4°C (wet ice) in dark. Minimize head space.	NA
Stormwater (untreated)	2 L	2 L fluorinated HDPE	4°C (wet ice) in a cooler Minimize head space.	NA
Coho Acute Toxicity	20 L	20L Fluorinated HDPE	4°C (wet ice) in dark. Minimize head space.	Initiate test within 36 hours (refer to contingencies in the event coho have not sufficiently developed)
6PPD-quinone	250 mL	250 mL amber glass	4°C (wet ice) in dark. Minimize head space, do not freeze.	4 weeks.
Dissolved organic carbon (KCEL)	50 mL	125 mL amber glass	Filter through 0.45 µm filter then HCl to pH ≤ 2 within 1 day, ≤6°C	28 days
Total Suspended Solids (KCEL)	1 L	1 L WM HDPE	≤6°C	7 days

Sample packaging and transport: Stormwater will be collected from Valve 2 (V2; Figure 2, Figure 3) in subsamples of 20 L, using fluorinated HDPE containers. Twenty three containers will be required to collect the full volume needed for the experiment (455 L). The 20L fluorinated HDPE stormwater sample containers will be filled to maximum capacity and an effort will be made to minimize headspace when capping. Full containers will be placed in an individual containment vessel (example below) and packed with wet ice. A black tarp or other dark barrier will cover all samples to minimize the potential for light exposure and photodegradation. Sample containers will be secured to the vehicle to eliminate safety risks during transport to bioretention laboratory.

Equipment Checklist. A sampling equipment list is provided in Attachment A.

Bioretention Laboratory. A schematic of the bioretention experimental facility is provided in Figure 6. The mixing and distribution tanks, as well as 12 soil columns and related pumps and conduits are shown. There will be three replicates of each HPBSMx and three of 60/40 BSM tested in each storm cycle. Sampling of treated effluents will be conducted at discrete sampling ports for each of the individual columns; effluent sample compositing necessary for use in toxicity tests will be performed in the Bioretention Laboratory. The array includes a sampling port (a conduit that does not drain to one of the soil columns) where untreated sample influents will be sampled (Figure 6).

Sampling Teams
For each storm cycle, FSU staff will deploy during daylight hours to the stormwater sampling location (Figure 1).

- There will be one team consisting of at least 3 people.
    - One of the FSU staff will deliver the grab sample of stormwater to KCEL for analysis of 6PPD-Q immediately after collection.
    - The other members of the team will drive the stormwater sample to the Bioretention Laboratory in Bellingham.
    - Prior to sample transport, 1 of the 3 team members will collect water quality parameters of the stormwater grab sample.

Sample Labeling. All samples collected for this program will be assigned a King County pre-login number[3] by KCEL's Laboratory Project Manager (Table 1). Labels will be pre-printed by KCEL.

The **sampling design for each storm** consists of:

[3] A pre-login number is a 5- digit code, preceded by "P" and followed by a "-n" with "n" indicating the individual sample number in a series (e.g., -1, -2, etc.). The code is preceded by "P" before samples are logged in by KCEL. Following login, the P becomes an "L".

- A set of twenty three 20-L subsamples of one 455 L stormwater sample for use in bioretention experiments
- A co-located and synoptic grab sample of stormwater to be delivered to KCEL immediately after collection and analyzed for 6PPD-Q; water quality parameters using probes will be measured on this grab.
    - The stormwater grab sample is discrete and not equivalent to the composite that will be prepared in the Bioretention Laboratory, so will have a unique pre-login number (PXXXXX-*n*, where *n* = 1 – 99).
    - An additional 2 L sample of the grab will be transported to the Bioretention Laboratory to undergo measurements and subsampling in that laboratory.

Once the 23 carboys of stormwater are delivered to the Bioretention Laboratory, the sample to be used for testing will be created by compositing and homogenizing the 23 subsamples in a mixing tank (Figure 6). That homogenate constitutes the "influent" for the bioretention soil columns. Also, each bioretention treatment type will generate a discrete sample. Samples to be collected in the Bioretention Laboratory are as follows:

- Samples of homogenized influent (PYYYYY-*n*)
    - Discrete samples from the influent sampling port for analysis of 6PPD-Q, TSS and DOC analysis, and for measurement of water quality parameters
        - 0.25 L aliquot will be collected for analysis of 6PPD-Q
        - 0.125 L aliquot will be collected for analysis of DOC
        - 1 L aliquot will be collected for analysis of TSS
        - 0.3-0.5 L sample will be placed in a wide mouth container (e.g., beaker) and water quality characteristics will be recorded.
    - Three replicates of the influent samples listed above will be collected, at the beginning, middle, and end of the process of delivering influent to the bioretention columns (N= 3 for each influent parameter).
- Samples of treated effluent from each sampling port shown in Figure 6 (PZZZZZ-*n*).
    - Discrete samples <u>from each effluent port</u> for analysis of 6PPD-Q, TSS, and DOC analysis, for measurement of water quality parameters, and for the effluent composite sample.
        - 0.25 L aliquot will be collected for analysis of 6PPD-Q
        - 1 L aliquot will be collected for analysis of TSS
        - 0.125 L aliquot will be collected for analysis of DOC
        - 0.3 L sample will be placed in a wide mouth container (e.g., beaker) and water quality characteristics will be recorded. These measurements may also be recorded directly from the full effluent sampling vessel, after other aliquots have been removed.
        - 6.6 L aliquot will be collected and used in 3-part composite of stormwater effluent for each treatment type.
    - Composites of treated effluents from each set of 3 bioretention treatment replicates, each composite will be assigned a unique pre-login number.

- At KCEL, effluent composites of 20 L will be split into subsamples, as follows:
    - One 0.25 L aliquot will be collected for analysis of 6PPD-Q
    - One 0.125 L aliquot will be collected for analysis of DOC
    - One 1 L aliquot will be collected for the analysis of TSS
    - One 0.3 L sample will be placed in a beaker and water quality characteristics will be recorded
    - The remaining volume of the 20 L composite will be collected for toxicity testing.

Effluent Sampling and Compositing Procedures
All effluents from each of the bioretention media columns will be collected. From each of the final effluent (following completion of all water transit through the bioretention columns), a 6.5 L aliquot will be removed and added to a clean 20 L fluorinated HDPE container. Each 6.5 L will be subsampled, as described in the "sampling design for each storm" section, above. In addition, the remainder of the final effluent (the volume not composited) will be sampled as discrete effluents for testing and water quality measurements, as described in the "sampling design for each storm" section, above.

KCEL will print labels in advance of each field sampling event. Each label will show the login number, locator, sampling date, and sample matrix. Sampling dates on pre-printed labels are likely to be incorrect, the correct dates will be provided on the field sheets. Field sheets will serve as the chain of custody for this project.

Prior to initiation of the project, a spreadsheet will be created listing all samples, locators and the measurements and analysis steps to be performed for each. Field staff will use this spreadsheet to ensure all measurements are effectively collected.

Field Notes

The QAPP requires minimal note-taking – See Section 6 of the QAPP. Field sheets generated by KCEL's Laboratory Information Management System (LIMS) will be used at all stations and will include the following information:

1. Login number
2. Locator
3. Date and time of sample collection
4. Initials of all sampling personnel
5. Water quality parameters (pH, temperature, DO, specific conductance and ORP)
6. Laboratory analysis required

The field sheet will contain records of sampling date and collection time, general weather, and the names of field crew and those performing measurements. Additional noteworthy observations include any deviations from the sampling plan, including changes in timing, sample

handling, excessively warm ambient outdoor temperatures (> 45°F), and unexpectedly high turbidity in the stormwater sample.

Data Collection, Water Quality Parameters

Throughout the experimental process of each storm cycle, the Field Team will be responsible for measurement of water quality parameters (pH, temperature, DO, specific conductance and ORP) in discrete subsamples. These data are collected at specified time points (Table 3).

Table 3. Time Point Definitions

Time Point	Definition	Location
T_0	Time stormwater is collected	Sampling location in Seattle
T_1	Time that stormwater sample is composited and homogenized	Bioretention Laboratory
T_2	Time that treatment is complete and effluents are sampled	Bioretention Laboratory
T_3	Time all samples arrive at KCEL	KCEL Receiving
T_4	Time that toxicity tests are conducted	KCEL Toxicity and Chemistry Labs

Stormwater characteristics will be measured throughout the experiment, at the time points shown in Table 4.

Table 4. Schedule for Measurement of Water Quality Parameters

Parameter	Time	6PPD-Q TSS and DOC	Water Quality Parameters
Experimental process point			
Untreated stormwater grab			
Stormwater sample grab, delivered to KCEL immediately	T_0	1	1
Stormwater sample grab in Bioretention Laboratory at time of influent compositing	T_1	0	1
Stormwater sample grab upon arrival at KCEL after bioretention test	T_3	1[a]	1
Untreated stormwater composited into influent for treatment			
Composited stormwater influent in Bioretention Laboratory at time of compositing	T_1	3	3
Untreated stormwater composite, upon arrival at KCEL after bioretention test	T_3	0	1
At the point of toxicity testing	T_4	1	1
Treated stormwater			
Post treatment effluent, at the time of sample collection in bioretention laboratory	T_2	12[b]	12
Treated stormwater composites, upon arrival at KCEL after bioretention test	T_3	0	4
At the point of toxicity testing	T_4	4	4

[a] Only 6PPD-Q will be analyzed. TSS and DOC will not be analyzed.
[b] 6PPD-Q and TSS only will be analyzed

For each sample for which these measurements are collected, an aliquot of 0.3 to 0.5 L will be poured into a clean 500 ml beaker or other container. All water quality parameters will be measured and recorded in each sample prior to moving to the next sample. Probes will be rinsed with DI water between samples, consistent with SOPs and manufacturer instructions.

Contingency Plans

There are two potential situations that require contingency plans for the field team: 1) insufficient flow at the sampling location, 2) insufficient (too low) concentrations of 6PPD-Q.

Contingency Plan Situation 1

If there is insufficient flow, sampling will include the use of a pump. A heavy duty submersible bilge pump would be lowered into the flow splitting vault (Figure 5) and water would be pumped into the stormwater sample containers.

Contingency Plan Situation 2

At the time of sampling, a stormwater grab sample will be collected and immediately transferred to KCEL for analysis of 6PPD-Q. Results will be used to confirm that the concentration of 6PPD-Q is ≥ 0.10 µg/L prior to commencing the bioretention media experiment. If the concentration is below this level, the process will be terminated and the experiment will be rescheduled. The stormwater in the sample bottles will be disposed.

Health and Safety

Protection of worker health and safety must be prioritized during all field work. The following hazards will be managed in the field:

- Field safety vest, close toed shoes, and Nitrile gloves (or equivalent) are required during sampling.
- Transportation to and from the Bellingham Lab will require securing carboys into the vehicle. If samples are being hauled in an open bed pickup an additional a cargo net will cover the entire load.

cc: Jean Power, FSU Manager, WLRD, DNRP
Susannah Rowles, KCEL Laboratory Project Manager, WLRD, DNRP

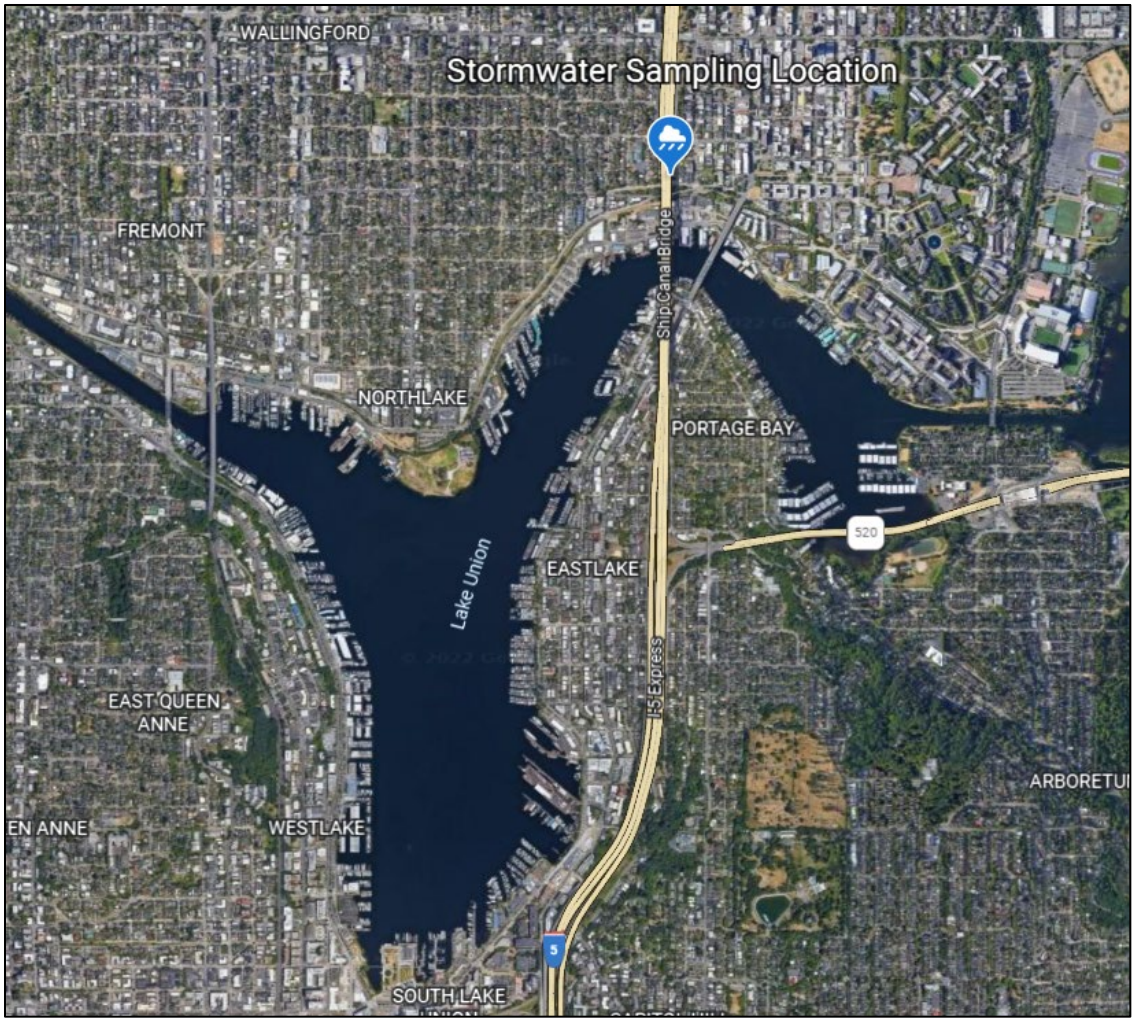

Figure 1. Sampling Location

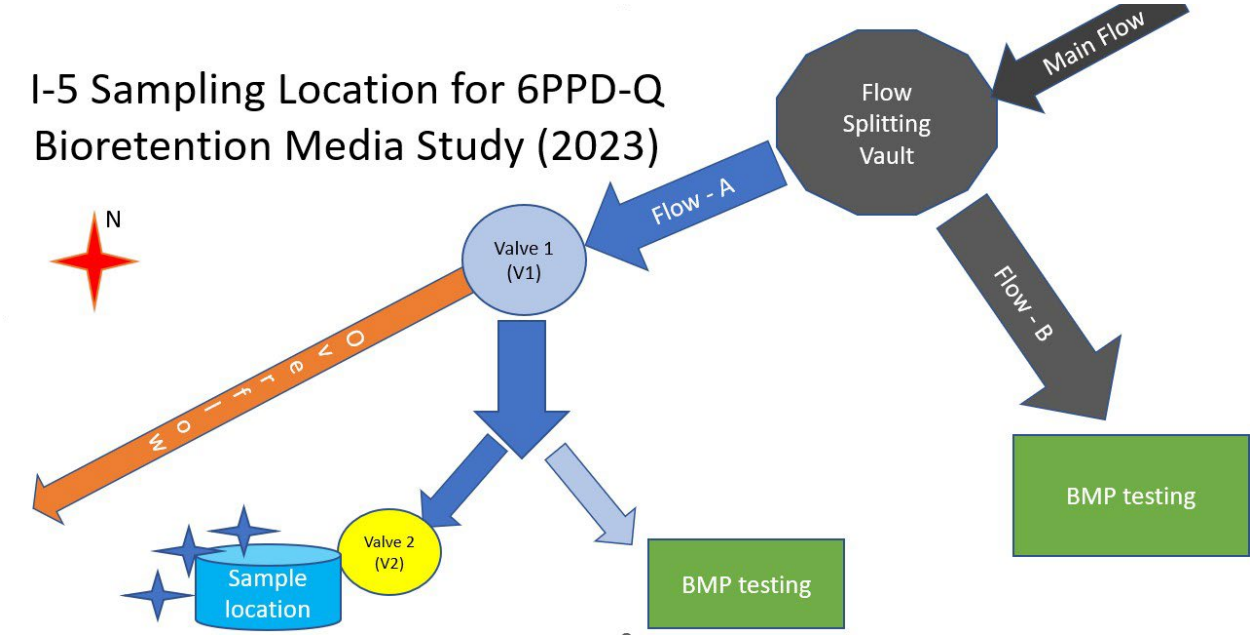

Figure 2. Sampling Location Schematic

Figure 3. Sampling Location, View from North to South

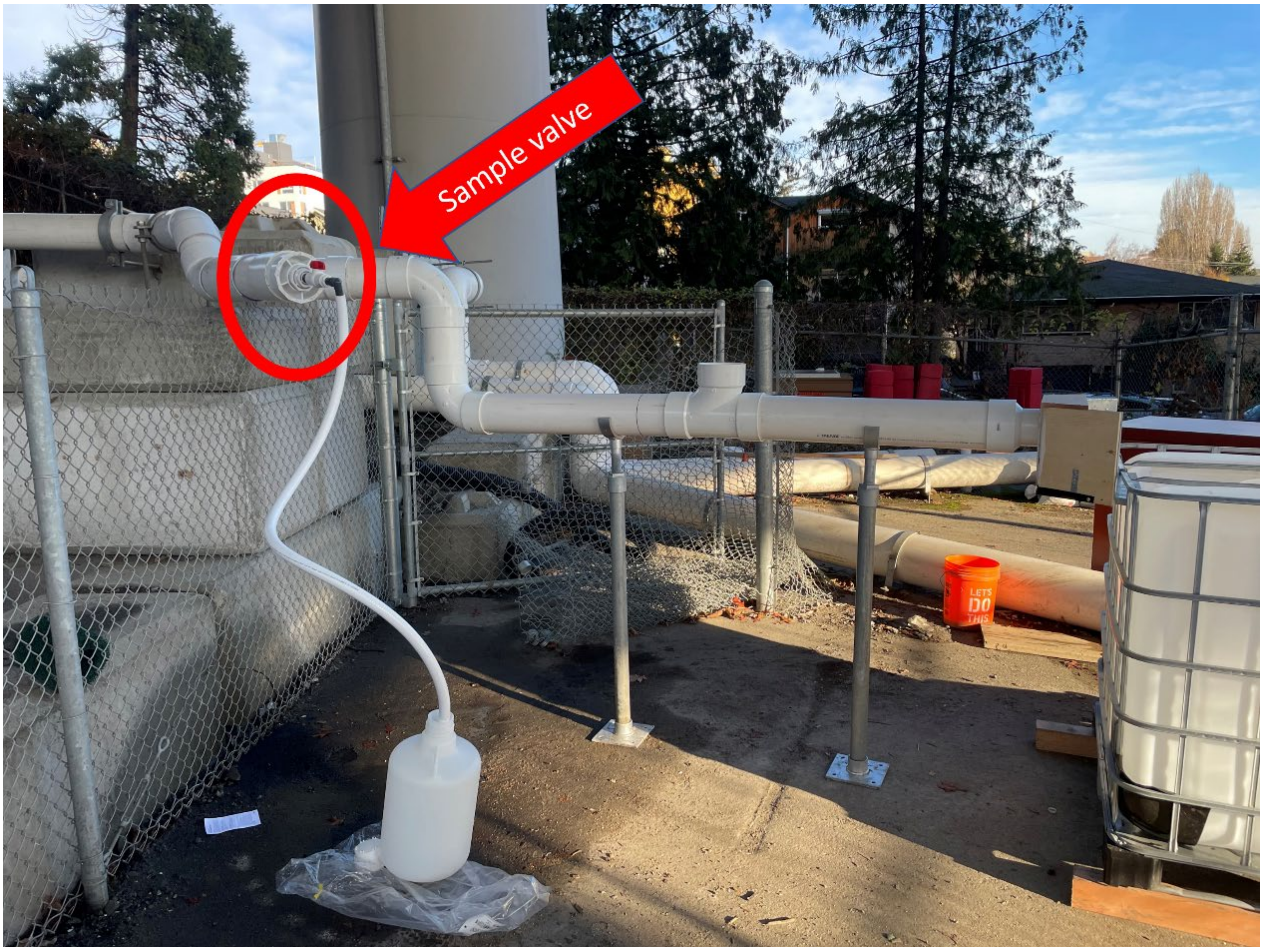

Figure 4. Sampling Valve and Illustration of Sample Collection

Figure 5. Location of Alternative Access Point for Stormwater Sampling

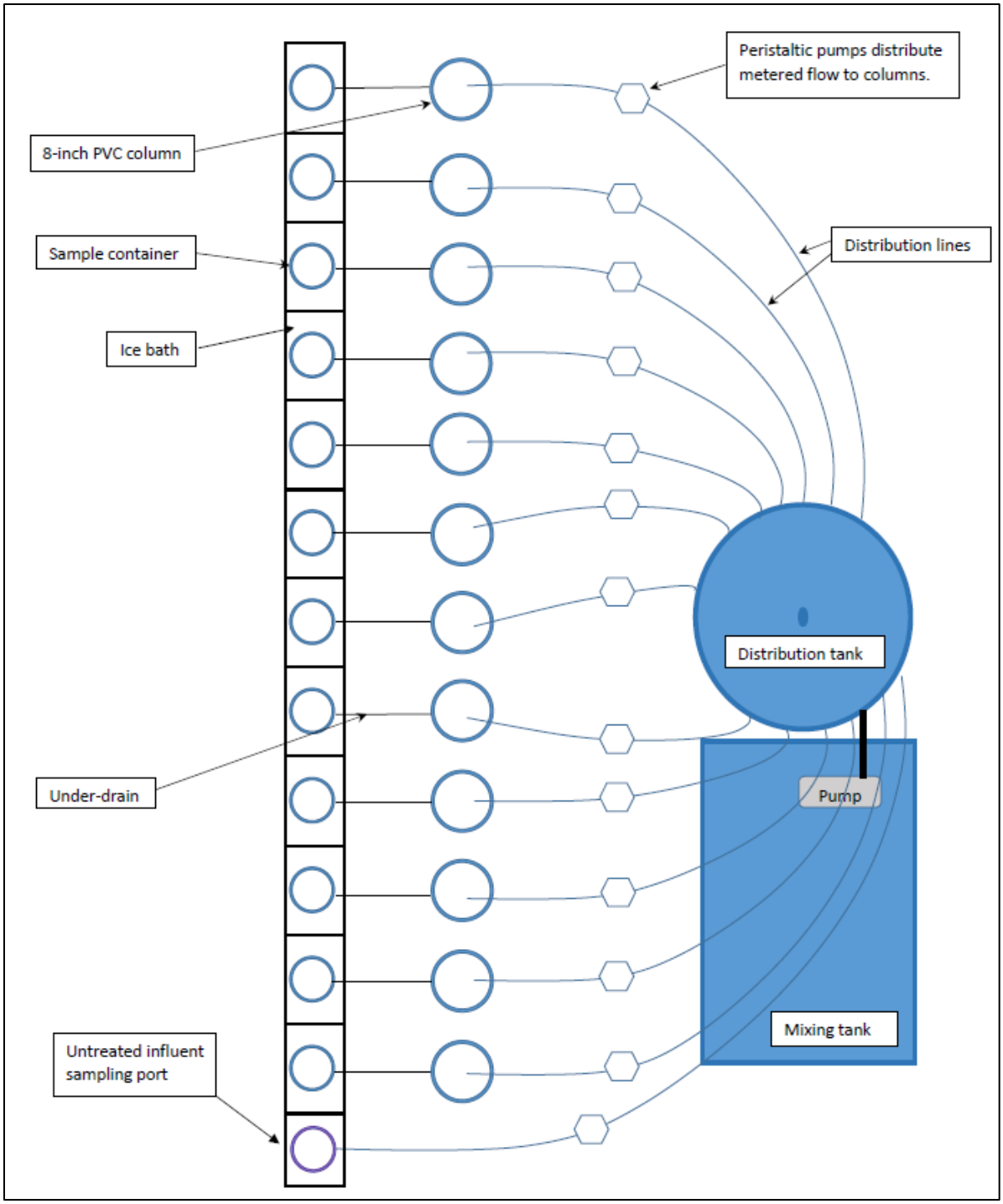

Figure 6. Schematic of Bioretention Media Column Array

Appendix B

Attachment A
Equipment Checklist
Sampling and Splitting

Stormwater sampling

☐ Field sheets/clipboard/waterproof pen	☐ Gate code: "9080"
☐ Gloves	☐ Reflective orange safety vest
☐ Driving Directions/Site maps	☐ Close toed shoes/boots
☐ Bottle Setups with Spare Bottles	☐ Phone/camera
☐ Coolers/ice/ice barrier/covers	☐ Warm clothing/spares
☐ Stormwater Sample Carboys (25)	☐ _____
☐ Calibrated YSI sonde	☐ _____
☐ Calibrated Hanna ORP instrument	☐ _____

Bioretention Lab & Sample Splitting Equipment

☐ Field sheets/clipboard/waterproof pen	☐ RO water squirt bottle
☐ Gloves	☐
☐ Bottle Setups with Spare Bottles	☐
☐ Coolers/ice/ice barrier/covers	☐
☐ Calibrated YSI sonde	☐
☐ Calibrated Hanna ORP instrument	☐ _____
☐ Magnetic stir plate & stir bars	☐ _____
☐ Beaker for reactivity readings	☐ _____

Appendix C. Standard Operating Procedures

The standard operating procedures to be applied in this project are listed below. Copies of SOPs are available upon request.

Parameter	SOP
Standard Operating Procedures - Water Quality Measurements	
Temperature (°C)	SOP #245v1
Specific conductance (or conductivity) (mS/cm)	SOP #245v1
pH (unitless)	SOP #245v1
Oxidation-reduction potential (mV)	Hanna H198190 user manual
Dissolved oxygen (mg/L)	SOP #245v1
Standard Operating Procedures - Analytical and Toxicity Testing	
6PPD-quinone by LCMS/MS	KCEL SOP #4077:
Rainbow Trout Acute Toxicity Test (modified for coho)	KCEL SOP #406v3
Total suspended solids	KCEL SOP #3009 and SM 2540-D
Dissolved organic carbon	KCEL SOP #3036 and SM 5310-B
Fathead Minnow Acute Toxicity Test	KCEL SOP #414v3

Appendix D. Field Sheet Example

Login: L80791 **Streams NZMS January 2023** **FSU TC: _____**
Project: 421240A **LPM: Colin Elliott**

CHAIN OF CUSTODY

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

Sample Number	**L80791-1**	**L80791-2**	**L80791-3**
QC Link			
Locator	**A320**	**0440**	**0442**
Short Loc Desc	BIG SOOS	MAY CR	COAL CR
Locator Desc	BIG SOOS CREEK//USGS GAGING STATION 12112600 .25 MI UPST OF	MAY CREEK//GAGING STATION NEAR BRIDGE ON LAKE WASHINGTON BLV	COAL CREEK IN COAL CREEK NATURAL AREA
Site	STREAMS	STREAMS	STREAMS
Comments			
Start Date/Time	01-11-2023	01-11-2023	01-11-2023
End Date/Time			
Time Span			
Sample Depth			
COND, FIELD			
DO, FIELD			
PERSONNEL			
PH, FIELD			
SAMP FUNC	**********	**********	**********
SAMP METH			
SAMP TEMP			
Dept, Matrix, Prod (Cont ID)	3 LK ALK; TURB (52) 3 LK NH3; NO23; ORTHOP (31) 3 LK TOTN; TOTP (41) 3 LK TSS (13) 5 LK MODEC-MF (54)	3 LK ALK; TURB (52) 3 LK NH3; NO23; ORTHOP; SI (31) 3 LK TOTN; TOTP (41) 3 LK TSS (6) 5 LK FC-MF; MODEC-MF (54)	3 LK ALK; TURB (52) 3 LK NH3; NO23; ORTHOP (31) 3 LK TOTN; TOTP (41) 3 LK TSS (6) 5 LK MODEC-MF (54)

Appendix E: Glossaries, Acronyms, and Abbreviations

Glossary of General Terms

Ambient: Background or away from point sources of contamination. Surrounding environmental condition.

Anthropogenic: Human-caused.

Conductivity: A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

Dissolved oxygen (DO): A measure of the amount of oxygen dissolved in water.

Effluent: An outflowing of water from a natural body of water or from a human-made structure. For example, the treated outflow from a wastewater treatment plant.

Nutrient: Substance such as carbon, nitrogen, and phosphorus used by organisms to live and grow. Too many nutrients in the water can promote algal blooms and rob the water of oxygen vital to aquatic organisms.

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

Pollution: Contamination or other alteration of the physical, chemical, or biological properties of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will, or are likely to create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

Salmonid: Fish that belong to the family *Salmonidae*. Species of salmon, trout, or char.

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

Synoptic: Data collected simultaneously or over a short period of time.

Total suspended solids (TSS): Portion of solids retained by a filter.

Turbidity: A measure of water clarity. High levels of turbidity can have a negative impact on aquatic life.

90th percentile: An estimated portion of a sample population based on a statistical determination of distribution characteristics. The 90th percentile value is a statistically derived estimate of the division between 90% of samples, which should be less than the value, and 10% of samples, which are expected to exceed the value.

Acronyms and Abbreviations

6PPD-Q	6PPD-Quinone (2-anilino-5-(4-methylpentan-2-ylamino)cyclohexa-2,5-diene-1,4-dione)
BSM	Bioretention soil media
CA	Contributing area
CAE	Contributing area effectiveness
DI	Deionized
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DQO	data quality objectives
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
et al.	And others
FSA	Facility surface area
FSP	Field sampling plan
FSU	Field Sciences Unit
GIS	Geographic Information System software
GPS	Global Positioning System
HDPE	High density polyethylene
FHDPE	Fluorinated HDPE
HPBSM	high performance bioretention soil media
KCEL	King County Environmental Laboratory
L	Liter
LID	Low-Impact Development
LIMS	Laboratory information management system
LC_{20}	Concentration lethal to 20 percent of the exposed population
LC_{50}	Concentration lethal to 50 percent of the exposed population
MDL	Method detection limit
MQO	Measurement quality objective
MS/MSD	Matrix spike/matrix spike duplicate
OP	Ortho phosphorus
PD	Precipitation depth
PQL	Practical quantitation limit
QA	Quality assurance
QC	Quality control
QAPP	Quality assurance project plan
RL	Reporting limit
RPD	Relative percent difference
RSD	Relative standard deviation
RTR	Runoff treatment requirement
SOP	Standard operating procedure
SPE	Solid phase extraction
SPLP	Synthetic precipitation leaching procedure
SRM	Standard reference materials

SWS	King County Stormwater Services Section
TOC	Total organic carbon
TP	Total phosphorus
TSS	Total suspended solids
URMS	Urban runoff mortality syndrome
WM	Wide mouth

Units of Measurement

°C	degrees centigrade
cm	centimeter
dw	dry weight
ft	feet
g	gram, a unit of mass
kg	kilograms, a unit of mass equal to 1,000 grams
kg/d	kilograms per day
m	meter
mm	millimeter
mg	milligram
mg/kg	milligrams per kilogram (parts per million)
mg/L	milligrams per liter (parts per million)
mL	milliliter
mS/cm	milli siemens per centimeter, a unit of conductivity
mV	millivolts
ng/g	nanograms per gram (parts per billion)
ng/kg	nanograms per kilogram (parts per trillion)
ng/L	nanograms per liter (parts per trillion)
pg/g	picograms per gram (parts per trillion)
pg/L	picograms per liter (parts per quadrillion)
s.u.	standard units
µg/g	micrograms per gram (parts per million)
µg/kg	micrograms per kilogram (parts per billion)
µg/L	micrograms per liter (parts per billion)
µm	micrometer
µM	micromolar (a chemistry unit)
µmhos/cm	micromhos per centimeter
ww	wet weight

Quality Assurance Glossary

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

Accuracy: The degree to which a measured value agrees with the true value of the measured property. USEPA recommends that this term not be used, and that the terms *precision* and *bias* be used to convey the information associated with the term *accuracy* (USEPA, 2014).

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

Bias: Discrepancy between the expected value of an estimator and the population parameter being estimated (Gilbert, 1987; USEPA, 2014).

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

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

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

Comparability: The degree to which different methods, data sets and/or decisions agree or can be represented as similar; a data quality indicator (USEPA, 2014; USEPA, 2020).

Completeness: The amount of valid data obtained from a project compared to the planned amount. Usually expressed as a percentage. A data quality indicator (USEPA, 2014; USEPA 2020).

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

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

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

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

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

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

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

Data validation: The process of determining that the data satisfy the requirements as defined by the data user (USEPA, 2020). There are various levels of data validation (USEPA, 2009).

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

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

Duplicate samples: Two samples taken from and representative of the same population, and carried through and steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variability of all method activities including sampling and analysis (USEPA, 2014).

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

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

Laboratory Control Sample (LCS)/LCS duplicate: A sample of known composition prepared using contaminant-free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern. It is prepared and analyzed in the same batch of regular samples using the same sample preparation method, reagents, and analytical methods employed for regular samples. Monitors a lab's performance for bias and precision (USEPA, 2014).

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

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

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

Method: A formalized group of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, data analysis), systematically presented in the order in which they are to be executed (USEPA, 2001).

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

Method Detection Limit (MDL): The minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results (USEPA, 2016). MDL is a measure of the capability of an analytical method of distinguished samples that do not contain a specific analyte from a sample that contains a low concentration of the analyte (USEPA, 2020).

Minimum level: Either the sample concentration equivalent to the lowest calibration point in a method or a multiple of the method detection limit (MDL), whichever is higher. For the purposes of NPDES compliance monitoring, EPA considers the following terms to be synonymous: “quantitation limit,” “reporting limit,” and “minimum level” (40 CFR 136).

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

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

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

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

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

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

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

$$\mathrm{RPD} = [\mathrm{Abs}(a\text{-}b)/((a + b)/2)] * 100\%$$

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

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

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

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

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

Reporting level: Unless specified otherwise by a regulatory authority or in a discharge permit, results for analytes that meet the identification criteria (i.e., rules for determining qualitative presence/absence of an analyte) are reported down to the concentration of the minimum level established by the laboratory through calibration of the instrument. EPA considers the terms "reporting limit," "quantitation limit," and "minimum level" to be synonymous (40 CFR 136).

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

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

Sample (statistical): A finite part or subset of a statistical population (USEPA, 1992).

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

Spiked blank: A specified amount of reagent blank fortified with a known mass of the target analyte(s); usually used to assess the recovery efficiency of the method (USEPA, 2014).

Spiked sample: A sample prepared by adding a known mass of target analyte(s) to a specified amount of matrix sample for which an independent estimate of target analyte(s) concentration is available. Spiked samples can be used to determine the effect of the matrix on a method's recovery efficiency (USEPA, 2014).

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

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

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

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

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