The Use of Unamended Soils for Treatment of 6PPDQ in Stormwater: Persistence, Soil Types, and Influence of Vegatation

Quality Assurance Project Plan

By

EA Engineering, Science, and Technology, Inc., PBC

For the

Water Quality Program

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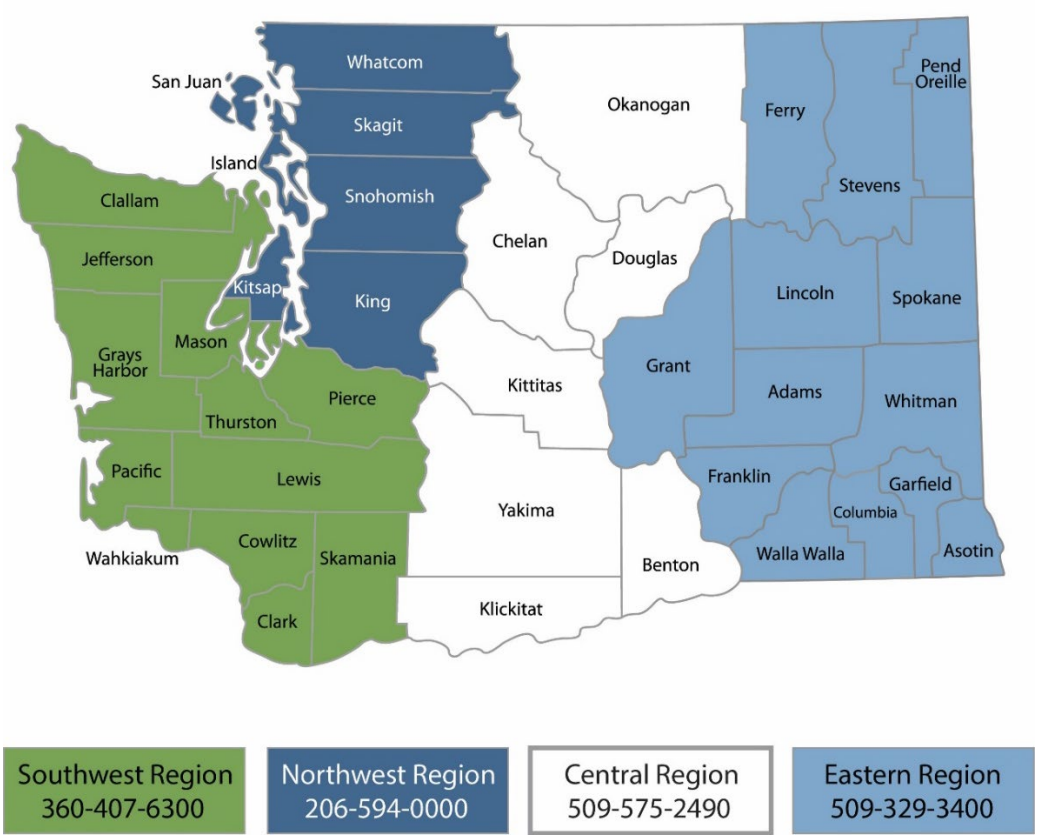

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DEPARTMENT OF
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November 2024

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EAP: Environmental Assessment Program

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Executive Summary

Recent studies have identified the tire wear particle (TWP) associated contaminant, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine-quinone (6PPD-quinone or "6PPDQ"), as a driver of increased salmonid mortality in urbanized watersheds. Consequently, significant scientific and regulatory interest has been placed on the reduction of 6PPDQ and other contaminants in urban stormwaters. A recent review conducted by the Washington State Department of Ecology (hereafter referred to as Ecology) evaluated the efficacy of various best management practices (BMPs) for reducing 6PPDQ. This report and subject matter experts at Ecology identified priority data gaps for further research. One such data gap was the potential use of unamended soils for 6PPDQ reduction, as well as the persistence of 6PPDQ within these soils. Unamended soils utilize on-site natural features to provide stormwater reduction benefits, therefore representing a potential low impact development (LID) BMP for mitigation of 6PPDQ in stormwater. Furthermore, the use of vegetation in bioretention systems was identified as another potential BMP that is limited by a lack of empirical data regarding the efficacy of soil-vegetation mixes for 6PPDQ reduction.

Taking this into account, the study described within this quality assurance project plan (QAPP) aims to determine the reduction of 6PPDQ and other stormwater contaminants (metals and PAHs) by three different unamended soil types, the persistence of 6PPDQ within unamended soils following their use in bioretention columns, and the efficacy of different soil-vegetation mixes for 6PPDQ reduction. A bioretention soil mix (BSM) recommended for use in Washington and previously shown to provide a reduction in 6PPDQ concentrations will be used to compare and contextualize the reduction provided by unamended soils. In addition, the soil-vegetation study will include a sterile and a non-sterile soil-only treatment to determine the influence of microbial communities on 6PPDQ reduction. All column studies will incorporate stormwater collected from a highly urbanized site in Lake Union, WA, that is commonly used in other stormwater BMP assessment studies.

This QAPP provides background information on the issue of 6PPDQ in stormwater, project goals and objectives, and detailed descriptions of both planned experiments. Data quality objectives and indicators are described, as well as the laboratory and field procedures involved. Overall, the outcomes of this study are anticipated to fill key data gaps regarding the management of 6PPDQ in stormwater and facilitate the use of unamended soils and soil-vegetation blends as LID BMPs for stormwater management.

Introduction

This quality assurance project plan (QAPP) describes a study to determine the efficacy of unamended soils and soil-vegetation bioretention columns in mitigating levels of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine-quinone (6PPD-quinone or "6PPDQ") in stormwater. The overarching goal of this project is to inform the potential use of unamended soils as best management practices (BMPs) for stormwater 6PPDQ mitigation. This project is funded by the Washington Department of Ecology (hereafter referred to as Ecology) through the Environmental Consulting Services statewide contract.

Background

Tire wear particles (TWP) contribute to pollutants such as microplastics and 6PPD, which may be transported to aquatic environments through stormwater runoff. Impacts to coho salmon from 6PPD, a tire anti-degradant, and its metabolite 6PPDQ in Washington State were first observed in the 1980s when monitoring surveys reported abnormal swimming behaviors and increased pre-spawning die-offs associated with more urbanized waterbodies (Scholz et al. 2011). Further studies elucidated a suite of organic contaminants in TWP leachates associated with salmon die-offs in urban streams (Peter et al. 2018), with the metabolite of 6PPD, 6PPDQ, ultimately identified as the primary driver of coho salmon mortality (Tien et al. 2021). Since these studies, 6PPD and 6PPDQ have been detected in a range of matrices globally, including roadside dust, terrestrial soils, atmospheric fine particles, and stormwater (Chen et al. 2023). Given that 6PPDQ has been shown to induce toxicity to salmonids at concentrations below those recorded in the environment (Tian et al. 2022), developing approaches to mitigate stormwater contamination is a priority.

In a recent review Ecology evaluated a suite of stormwater BMPs for their potential efficacy in reducing 6PPD and 6PPDQ, with knowledge gaps identified (Ecology 2022). A suite of BMPs were identified as having high potential to remove 6PPD and 6PPDQ, including street sweeping, bioretention, infiltration basins, and soil mixes, with additional BMPs including vegetation, modular wetlands, and vegetation identified as having medium potential effectiveness. One approach to address management of roadway related contaminants such as 6PPD and 6PPDQ is to invest in Low Impact Development (LID) BMPs. This approach employs designs that incorporate aspects of nature-based solutions, such as preservation of natural landscapes and utilization of plants for retention of pollutants. LID approaches offer the advantage of using on-site natural features to manage stormwater, including the use of unamended soil, tree retention, vegetated roofs, and rainwater harvesting. Due to their use of on-site natural features, LID approaches may be implemented more easily and may be more cost efficient as compared to specifically designed retention cells and other approaches. However, implementation of these approaches is limited by a lack of information regarding their efficacy in removal of 6PPD and 6PPDQ. For example, no studies to date have quantified the removal of 6PPD and 6PPDQ by unamended soils, with most research implementing modified soils such as high performance bioretention soil mixes (BSM, McIntyre et al. 2015, 2023).

Summary of previous studies

Previous studies focusing on bioretention of stormwater contaminants have employed amended soils to maximize contaminant reduction (McIntyre et al. 2023; Rodgers et al. 2023). McIntyre et al. (2023) utilized bioretention columns containing 60% sand, 40% compost, and a mulched bark topping to test the potential mitigation of stormwater toxicity to coho salmon. The authors found net removal of a suite of stormwater contaminants including PAHs, dissolved metals, and solids, and that biofiltration of runoff prevented acute mortality of coho salmon alevin (McIntyre et al. 2023). Though this experiment was conducted in 2015 prior to the discovery of 6PPDQ as a causative agent for salmon die-offs, mortality observed in juvenile salmon exposed to the unfiltered runoff appeared consistent with 6PPDQ exposure; thus, it is likely that bioretention removed 6PPD and 6PPDQ in this study. In another study, Rodgers et al. (2023) focused on the reduction of 6PPDQ in a functional bioretention system located in Vancouver, Canada. The bioretention systems included a sediment pad with bioretention media, mulch, and vegetation. The authors performed a spike and recovery experiment followed by one-dimensional multimedia modeling to determine the reduction of 6PPDQ loadings in runoff passing through bioretention cells. Overall, modeled data indicated that stormwater bioretention systems were capable of mitigating >90% of 6PPDQ loadings under typical conditions (Rodgers et al. 2023).

To the author's knowledge, no studies have considered the use of unamended soils in bioretention systems for 6PPDQ, or empirically determined the persistence of these contaminants in soil. Furthermore, few studies have measured 6PPDQ and other TWP-associated contaminants in field collected soils (Chen et al. 2023). Cao et al. (2022) studied TWP-associated contaminants in air particles, runoff water, and roadside soils from urbanized areas of Hong Kong, finding soil concentrations of 6PPDQ ranging from 9.50 – 936 ng/g. Comparatively, Zhang et al. (2024) found low concentrations of 6PPDQ in soils collected from around e-waste recycling areas in Guiyu and Haojiang, China, with concentrations < 1.0 ng/g. In addition, the uptake and potential accumulation of 6PPDQ by vegetation incorporated in bioretention systems has not been determined. Laboratory studies have demonstrated the uptake of TWP-associated contaminants including 6PPD, 6PPDQ, and 1,3-diphenylguanidine in lettuce, *Valerianella locusta* L (Castan et al. 2022), with a subsequent study of leafy vegetables collected from Switzerland and Israel finding no detections of 6PPDQ (Sherman et al. 2024).

As previously mentioned, no empirical studies have determined the persistence of 6PPDQ in soils to the author's knowledge. However, Xu et al. (2023) studied the fate of 6PPDQ in flooded and wet soils during TWP aging, finding that concentrations of 6PPDQ in soil significantly declined after 3 days in wet soils, though 30 days were needed to observe a significant decrease in flooded soils. The authors concluded that biodegradation dominated the fate of 6PPDQ under normal, wet, conditions, but flooding was conducive to formation of 6PPDQ during TWP aging and longer overall persistence (Xu et al. 2023). Soils utilized in bioretention systems will likely be subject to repeated cycles of flooding and drought conditions; thus, determining the persistence of 6PPDQ in soils following their use in a simulated bioretention system is of importance.

Problem statement

Unamended soils represent a potential LID BMP for mitigation of 6PPDQ in stormwater. However, the use of these soils in potential bioretention systems is limited by a lack of information regarding their 6PPDQ reduction capacity and the potential persistence of 6PPDQ within soils. In addition, the efficacy of different soil-vegetation mixes and microbial communities in reducing 6PPDQ contamination has not been empirically studied with column experiments.

Scope and Purpose

This QAPP outlines the methods the EA project team will use to achieve the project goals described below and provide recommendations to Ecology regarding the use of unamended soils for 6PPDQ mitigation. It includes a project description, experimental processes and tasks, project organization and schedule, data quality objectives, field and laboratory procedures, quality control procedures, data management, and data verification methods.

Project Description

The present study aims to determine the efficacy of unamended soils and soil-vegetation columns for 6PPDQ mitigation in stormwater, as well as the potential persistence of these contaminants in bioretention systems. In addition, this project aims to determine the costs associated with implementation and maintenance of using unamended soils as BMPs using life cycle analysis.

Project goals

The goals of this project are as follows:

- Quantify the reduction of 6PPDQ by three unamended soils with different characteristics (e.g., cation exchange capacity [CEC], percent organic carbon, particle size) relative to a BSM
- Determine the longevity of 6PPDQ in unamended soils and BSM following use for stormwater mitigation
- Evaluate the reduction of 6PPDQ in soil-vegetation systems with different vegetation mixes
- Assess uptake of 6PPDQ in vegetation following use for stormwater mitigation.

In addition, a secondary goal of the project is:

- Determine the relationship between 6PPDQ and other stormwater associated contaminants including metals and polycyclic aromatic hydrocarbons (PAHs) in field-collected stormwater samples.

Project location

Stormwater runoff samples will be collected from the Lake Union Ship Canal Test Facility (Lake Union, Seattle, WA), which is located under the Interstate-5 bridge at the northern end of Lake Union. This site is owned by the WA State Department of Transportation and is managed by Ecology and receives runoff from ~ 32 acres, including 23 acres of pavement and 9 acres of roadside landscaping. All runoff passes through catch basins prior to entering the stormwater collection system, where it is consolidated in a 30-inch pipe. The facility was constructed to enable testing of up to four stormwater treatment technologies simultaneously; thus, stormwater flow is diverted from the 30-inch pipe to the site using a half-pipe structure and a series of flow splitters. The facility has been used for stormwater collection for similar projects (King County 2023) and is currently used as a testing facility for stormwater treatment technologies. All laboratory studies will be conducted at EA's Ecotoxicology laboratory in Hunt Valley, MD.

Tasks required to conduct study

Table 1 below summarizes the tasks that will be required to conduct the project and meet the goals described above. A more detailed project schedule is provided in the Organization and Schedule section below.

Table 1. Proposed Project Tasks, Objectives, and Timeframes

Task	Objective	Proposed Timeframe
1. Develop and finalize QAPP	QAPP completed and approved by Ecology	September-October 2024
2. Prepare bioretention columns	Construct bioretention columns and perform flushing with deionized water.	October 2024
3. Collect and characterize soil samples	Collect different soil types for testing in bioretention columns, analyze soil characteristics.	October – November 2024
Task 4: Unamended Soil Persistence Study		
4a. Collect stormwater and initiate unamended soil testing	Collect stormwater, ship for chemical analysis and initiate testing by passing through bioretention columns.	November 2024
4b. Determine persistence and reduction of 6PPDQ in soil	Collect and analyze 6PPDQ in column effluent and in soil after ten stormwater applications	November 2024 – March 2025
Task 5: Soil-Vegetation Column Study		
5. Determine efficacy of different soil-vegetation mixes for 6PPDQ reduction	Apply collected stormwater to soil-vegetation systems, analyze reduction of 6PPDQ and uptake in vegetation	February 2025 – April 2025
6. Analysis of analytical chemistry data	Analyze all chemical data for 6PPDQ in various matrices, determine trends and half-lives	May 2025
7. Completion of Final Report & Economic Analysis	Synthesize all available data, provide recommendations to Ecology	May 2025 – June 2025

Experimental Processes and Tasks

This section describes the methods used for the laboratory column experiments. Field procedures will be described in further detail below. Overall, the experiment involves the following elements:

- Bioretention column construction, preparation and flushing
- Soil and stormwater sampling (described in further detail in the Field Procedures section)
- Unamended soil reduction and persistence studies
- Soil-vegetation column testing
- Chemical analysis of stormwater, soil, and vegetation samples

Bioretention column construction, preparation, and flushing

There are several quality assurance/quality control (QA/QC) topics associated with the construction of columns, including the potential for loss of 6PPDQ to materials such as plastics used in the bioretention column. As such, materials not known to sorb or leach 6PPDQ, such as polyvinyl chloride (PVC), will be used for construction of columns. PVC columns have been utilized in several similar studies of bioretention performance including McIntyre et al (2015, 2023) and King County (2023). Furthermore, columns will be flushed with deionized water prior to initiating the experiment and the effluent collected to determine any residual contamination of 6PPDQ, metals, and PAHs associated with the materials used. Columns will measure approximately 60 cm in height with a 15.2 cm diameter. The bottom of the column will be covered with Nitex nylon mesh with effluent draining directly into buckets for collection of effluent (Figure 1).

A total of 30 columns will be constructed to be used across all experiments: 12 for use in Task 4 (unamended soil study) and 18 for use in Task 5 (soil-vegetation study). Excluding peristaltic pumps used to provide a controlled flow rate to the bioretention columns, no shared materials will be used between Tasks 4 and 5 to avoid potential cross-contamination. Columns will be filled with soil to a depth of 45.7 cm (equivalent to 18 inches) following the recommendations in Ecology's Stormwater Management Manual for Western Washington (SMMWW, Ecology 2024) and compacted using a stainless-steel tamper. Prior to initiation of the experiments, all columns will be flushed with deionized water (5.1 L) and effluent collected to test for potential contamination associated with column materials.

Figure 1. Schematic of the Bioretention Columns for Tasks 4 and 5.

Soil and stormwater sampling

Specific details on field collections of soil and stormwater will be provided in the Field Procedures section below. This section will focus on the targeted soil types to be used for bioretention columns as well as the frequency and amounts of stormwater required to be collected.

Target soils for column studies

Soil mixes will be identified and developed using the Stormwater Management Manual for Western Washington's (SMMWW) site suitability criteria (SSC, V-5.6, Ecology 2024), which stipulates soil properties including infiltration rates and physical characteristics for siting infiltration BMPs with native soil. For example, SSC-4 and SSC-6 from the SMMWW identify an infiltration rate of ≤ 9 in/hr, a minimum organic carbon content of 1%, and a cation exchange capacity (CEC) of > 5 milliequivalents (mev) CEC/100g dry soil for native soils to be used in providing runoff treatment.

The soil types used for this objective will aim to meet these criteria and include a range of infiltration rates, percent organic carbon, and CEC to determine the importance of these factors for 6PPDQ retention in BMPs. Specifically, various soil types including loamy sand, sandy, and loam soils will be used since these are likely to differ in characteristics including organic carbon, mineral content, infiltration rates, and CECs. Estimated long-term infiltration rates for these soil types are provided in Table 2. Ecology's default bioretention soil mix will be used as the BSM for

comparison. Several bioretention studies have been conducted on Ecology's default soil mix (Herrera 2016, King County 2017, McIntyre et al. 2020); thus, this soil will serve as a control for the unamended and untested soils.

Table 2. Target Soil Types for Task 4.

Soil ID	Soil Type	Estimated Long-Term Infiltration Rate (cm/hr)
Unamended 1	Silt Loam	0.76[b]
Unamended 2	Clay Loam	0.15[b]
Unamended 3	Loam	0.33 [a]
BSM	Ecology's Default Bioretention Soil Mix	30.5

[a] Values are from SMMWW Volume III (2005)
[b] Values are from Minnesota Stormwater Manual
cm/hr = centimeters per hour
BSM = Bioretention Soil Mix

Details of specifications for BSM from the 2019 SMMWW are given below in Table 3.

Table 3. Specifications for the BSM.

Criteria	Target Range
Soil Properties	
Percent Sand (by volume)	60 - 65
Percent Compost (by volume)	35 – 40
Percent Organic Matter (by weight)	5-8
CEC	> 5 meq/100 g dry soil
Compost Properties	
pH	6.0 – 8.5
Percent Organic Matter	< 40
Soluble Salt Content (dS/cm)	< 4.0
Carbon to Nitrogen Ratio	< 25:1

CEC = Cation Exchange Capacity
dS/cm = Decisiemens per centimeter

Overall, adequate soil mass to fill all replicate columns to a depth of 45.7 cm (18 inches) will be collected, and a subsample of collected soils will be shipped to the contract laboratory for analysis of the following soil properties: pH, percent organic carbon, particle size, and CEC. The remaining soil will be shipped from Washington to Hunt Valley, MD, for use in column experiments. Further details on field collections and the amount of soil to be collected are provided in the Field Procedures section of this QAPP.

Stormwater influent rate and collections

To facilitate an understanding of the amount of stormwater required for this project, the influent volume of stormwater per column was calculated based on the following assumptions:

- A contributing area to bioretention facility surface area ratio (CA/FSA) of 15/1. This represents a bioretention facility area that is 6.7 percent of the total area contributing stormwater to the system (Jay et al. 2017, King County 2023).
- A contributing area effectiveness (CAE) of 90 percent. This represents 90 percent of the precipitation from the contributing area being delivered to the bioretention facility.
- A runoff treatment requirement (RTR) of 0.91. This corresponds to Ecology's requirement for the fraction of total stormwater by volume to undergo treatment in bioretention facilities
- A target precipitation depth (PD) of 2.29 cm. This is equivalent to a 24-hour storm with a return frequency of 0.2 years for the Seattle region.

These assumptions followed previous studies on bioretention designs in Western Washington (Jay et al. 2017, 2019; King County 2023; McIntyre et al. 2019) to facilitate comparisons with other studies. Based on these assumptions and the column dimensions listed above, the influent rate of stormwater per column was calculated as follows:

Input water volume (L) = column area (181 cm^2) x CA/FSA (15:1) x PD (2.29 cm) x CAE (0.90) x RTR (0.91)/1000 (cm^3/L)

Based on the above equation, a total of 5.1 L per column per stormwater event was calculated. For Task 4 (soil persistence), stormwater will be applied to a total of 12 columns at 5 different intervals, totaling 61.2 L of stormwater per event and a total of 306 L across all events. For Task 5 (soil-vegetation systems), stormwater will be applied to a total of 18 columns at 10 intervals, totaling 91.8 L of stormwater per event and a total of 918 L across all events. Stormwater will be applied to columns over a period of 8 hrs, equivalent to a rate of 10.6 mL/min (3.5 cm/hr). This rate is not anticipated to cause ponding within columns, is comparable with previous studies, and is classified as heavy rain (i.e., 1 – 5 cm/hr) according to the rainfall classification systems used in the United Kingdom and Canada (Environment Canada; McIntyre et al. 2019; United Kingdom Met Office 2012).

All stormwater samples will be collected from the Lake Union Ship Canal Test Facility, located close to the I-5 bridge in Lake Union, Seattle. This site has been used routinely in evaluations of stormwater BMP efficacy. Stormwater samples for use in experiments will be collected in high density polyethylene (HDPE) carboys for shipment to Hunt Valley, MD. A grab sample will also be taken at each stormwater sampling event to determine levels of 6PPDQ, and other contaminants including metals and PAHs. The grab sample will be separated into three aliquots for 6PPDQ, metal, and PAH analyses. Further details on stormwater sampling will be provided in the Field Procedures section below.

Unamended soil reduction and persistence studies

For this experiment, stormwater will be applied to columns containing one of four soil types described above to determine the 6PPDQ and stormwater contaminant reduction capacity. In addition, the persistence of 6PPDQ and other associated stormwater contaminants in soils following their use in bioretention columns will be determined. A schematic of the experiment is given below in Figure 2. Table 4 below describes the planned regime for stormwater application and sampling.

After receipt of stormwater samples from field collections, individual carboys containing stormwater will be combined within a 75.7 L (20 gallon) glass tank in a climate-controlled laboratory (set at 20 °C) and allowed to equilibrate. Following the equilibration period, stormwater will be pumped through each column at an approximate rate of 10.6 mL/min using peristaltic pumps, meaning influent will be applied for 8 hours. Peristaltic pumps will supply stormwater to a custom head that distributes the stormwater across each individual column evenly rather than a single stream.

Filtered effluent passed through soil columns will be collected directly in individual 18.9 L buckets for each column and sampled for analysis of 6PPDQ, metals, and PAHs. All 6PPDQ samples will be collected in 250 mL amber glass jars with PTFE caps, with 1L amber glass jars and 250 mL HDPE bottles used for PAHs and metals, respectively. This process will be repeated a total of five times over a period of 28 days. Samples will be shipped after each collection event on ice due to the short hold time for 6PPDQ (14 days for aqueous samples, EPA 2024).

Following the five stormwater events, soil (~ 10 g) will be sampled from each of the bioretention columns using a stainless-steel soil corer and added to 250 mL amber glass jars for 6PPDQ and PAH analysis, and 250 mL HDPE jars for metals. After the d0 soil sampling, bioretention columns will be sealed using plexiglass and no additional water will be applied during the over the course of the 120-d persistence study. Soil sampling will be conducted at d7, d15, d30, d60, d90, and d120 following stormwater application. To obtain a representative soil sample, three sub-samples from varying soil depths (0 -15 cm, 15 – 30 cm, and 30 – 45 cm) will be collected from each column by push corer and composited for 6PPDQ, metal, and PAH analysis.

Table 4. Timeline for Task 4 and Samples Generated

Activity	Day	Samples
Stormwater Application 1	0	Stormwater Filtered Effluent
Stormwater Application 2	7	Stormwater Filtered Effluent
Stormwater Application 3	14	Stormwater Filtered Effluent
Stormwater Application 4	21	Stormwater Filtered Effluent
Stormwater Application 5 & Soil Persistence d0	28	Stormwater Filtered Effluent
Soil Persistence d7	35	Soil
Soil Persistence d15	43	Soil
Soil Persistence d30	58	Soil
Soil Persistence d60	88	Soil
Soil Persistence d90	118	Soil
Soil Persistence d120	148	Soil

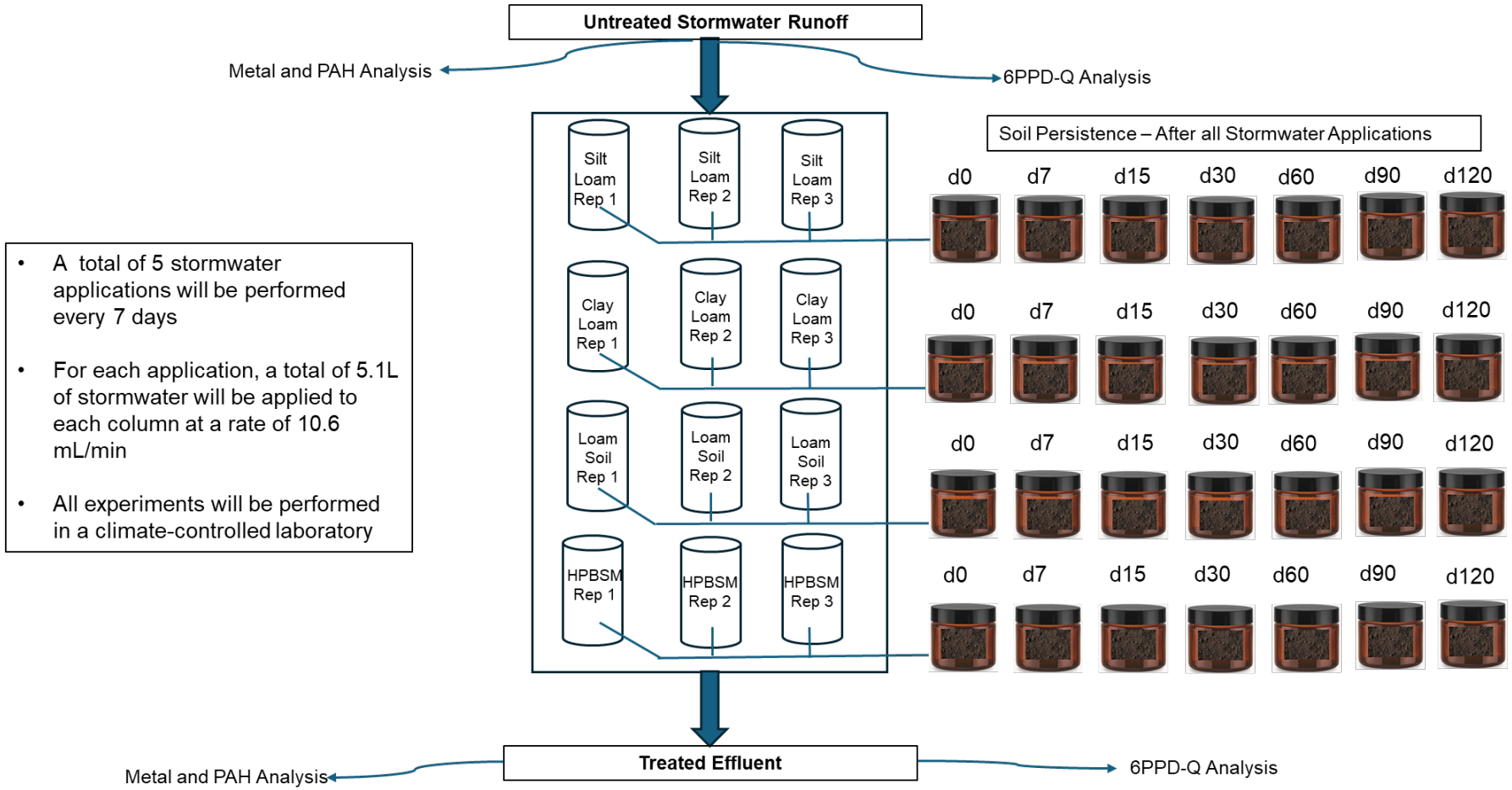

Figure 2. Schematic of the Unamended Soil Removal and Persistence Study (Task 4).

Soil-vegetation column testing

For this experiment, stormwater will be applied to columns containing various soil-vegetation mixes to determine the reduction of 6PPDQ, identify effective vegetation mixes, and determine potential uptake of 6PPDQ in vegetation (Figure 3). In addition, columns containing sterile soil or non-sterile soil only will be used to provide a comparison of the efficacy for 6PPDQ reduction when incorporating plants or microbes. The soil used for all columns will be the most effective soil in reducing 6PPDQ concentrations based on the results of Task 4. The specific vegetation blends to be used are described below in Table 5. These blends are recommended for use in wet biofiltration swales in the SMMWW and by the Washington State Department of Transportation (WSDOT, Ecology 2024) and have different characteristics in terms of drought tolerance, shade tolerance, and preferred habitat.

Table 5. Proposed Vegetation Mixes for Task 5

Treatment	Vegetation Used
Sterile Soil Only	None
Non-Sterile Soil Only	None
Vegetation Mix #1 (WSDOT Erosion Control Mix)	Perennial Ryegrass (*Lolium perenne)*, Creeping Red Fescue (*Festuca rubra*), White Dutch Clover (*Trifolium repens*)
Vegetation Mix #2 (SWMMWW Bioswale Seed Mix)	Tall fescue (*Festuca arundinacea*), Creeping bentgrass (*Agrostis stolonifera*), Redtop bentgrass (*Agrostis gigantea*)
Vegetation Mix #3 (SWMMM Wet Area Seed Mix)	Meadow fescue (*Festuca pratensis*), Meadow Foxtail (*Alopecurus pratensis*), Alsike Clover (*Trifolium hybridum*)

Bioretention columns used for the soil-vegetation experiments will be the same as those described previously, measuring 60 cm in height with a 15.2 cm diameter and mesh in the base to collect leachate. Columns will be filled with soil to a depth of 45.7 cm (equivalent to 18 inches) following the recommendations in the SMMWW (Ecology 2019). To ensure vegetation blends have adequate time to become established prior to initiating the experiment, seed mixes will be planted at project initiation in a commercially available soil and transplanted to columns when shoot lengths have reached ~ 10 cm. During the period of seedling growth, soil will be moisturized with deionized water daily and placed in an environmentally controlled room (20 ± 1 °C) with standardized light:dark cycles and temperature regimes. A total of four replicate columns for each treatment will be included.

Soils designated for the sterile treatment will be sterilized using three cycles of autoclaving and amended with three antibiotics (chloramphenicol, kanamycin, and cycloheximide) at an approximate concentration of 100 mg/kg of soil post-autoclaving (Liu et al. 2023). For the non-sterile soil treatment and the three vegetation treatments, subsamples of soil (2 g) will be taken from the upper 30 cm of the columns prior to initiating the experiment to determine microbial diversity using 16s ribosomal RNA (rRNA). Though soil microbial communities are known to vary with depth (Lopes et al. 2023), collected soil used for bioretention columns will represent the top 15 cm of soil (Field Procedures section); thus, no vertical sampling is required for microbial

diversity. Soil samples will be added to 50 mL borosilicate glass jars and 30 mL deionized sterilized water will be added prior to shipment to a contract laboratory for 16s rRNA analysis.

Prior to initiating the experiment, plant height and lateral area will be assessed in all bioretention columns containing vegetation to determine potential effects of stormwater application on plant growth. Plant height will be assessed for each individual species within a bioretention column and defined as the distance from the soil surface to the highest point. The plant lateral area will be calculated by measuring the maximum length and the perpendicular width of each plant and using the formula: Area = $\frac{Maximum\ Length}{2} * \frac{Perpendicular\ Width}{2} * \pi$ as described previously (Champagne-Caron et al. 2024).

To initiate the experiment, stormwater collected and shipped to EA will be allowed to equilibrate as described previously for Task 4. Following the equilibration period, stormwater will be pumped through each column at an approximate rate of 10.6 mL/min, meaning influent will be applied for 8 hours. All filtered effluent will be collected directly in individual 18.9 L buckets for each column and sampled for analysis of 6PPDQ, metals, and PAHs. All 6PPDQ samples will be collected in 250 mL amber glass jars with PTFE caps, with 1L amber glass jars and 250 mL HDPE bottles used for PAHs and metals, respectively.

As described in the table below, a total of ten stormwater applications will be performed following the methods described previously. At each stormwater application, stormwater samples and effluent following application to bioretention columns will be collected and shipped for analysis. After the fifth and tenth stormwater applications, subsamples of vegetation will be collected to determine potential bioaccumulation of 6PPDQ and stormwater contaminants. In addition, plant height and lateral area will be measured at these timepoints as described above to provide an assessment of plant growth, as well as soil for analysis of contaminant concentrations.

For the bioaccumulation component, a minimum of 5 g plant tissue (roots and shoots) will be collected from each plant species within a column, weighed, and transferred to a 30 mL amber vial for shipment to Texas Tech University (TTU) for analysis. If inadequate plant mass is available from within a particular column, tissue will be composited across replicate columns. Methods for extraction and instrumental analysis of plant samples will be described further in the Laboratory Procedures section below.

Following the ten stormwater applications, dechlorinated water (0.574 L) will be applied to each column once per week over a 30-day period. Following the 30 days, vegetation and soil will be sampled as described above to determine the persistence of 6PPDQ in these matrices after their use in bioretention systems. The interval between the final stormwater application and the soil/vegetation persistence sampling may be increased/decreased depending on the results of Task 4. For example, if data obtained from Task 4 indicates a short persistence time of 6PPDQ in soil (i.e., less than 30 days) following its use in a bioretention column, the length of time between cessation of the stormwater applications and the persistence sampling will be shortened.

Table 6. Proposed Timeline and Samples from Task 5.

Activity	Day	Samples
Stormwater Application 1	0	Stormwater Filtered Effluent
Stormwater Application 2	7	Stormwater Filtered Effluent
Stormwater Application 3	14	Stormwater Filtered Effluent
Stormwater Application 4	21	Stormwater Filtered Effluent
Stormwater Application 5, Vegetation Sampling/Growth Assessment, and Soil Sampling	28	Stormwater Filtered Effluent Roots Leaves Soil
Stormwater Application 6	35	Stormwater Filtered Effluent
Stormwater Application 7	42	Stormwater Filtered Effluent
Stormwater Application 8	49	Stormwater Filtered Effluent
Stormwater Application 9	56	Stormwater Filtered Effluent
Stormwater Application 10, Vegetation Sampling/Growth Assessment, and Soil Sampling	63	Stormwater Filtered Effluent Roots Leaves
Vegetation & Soil Sampling	93*	Soil Roots Leaves

* Subject to change based on the findings of Task 4.

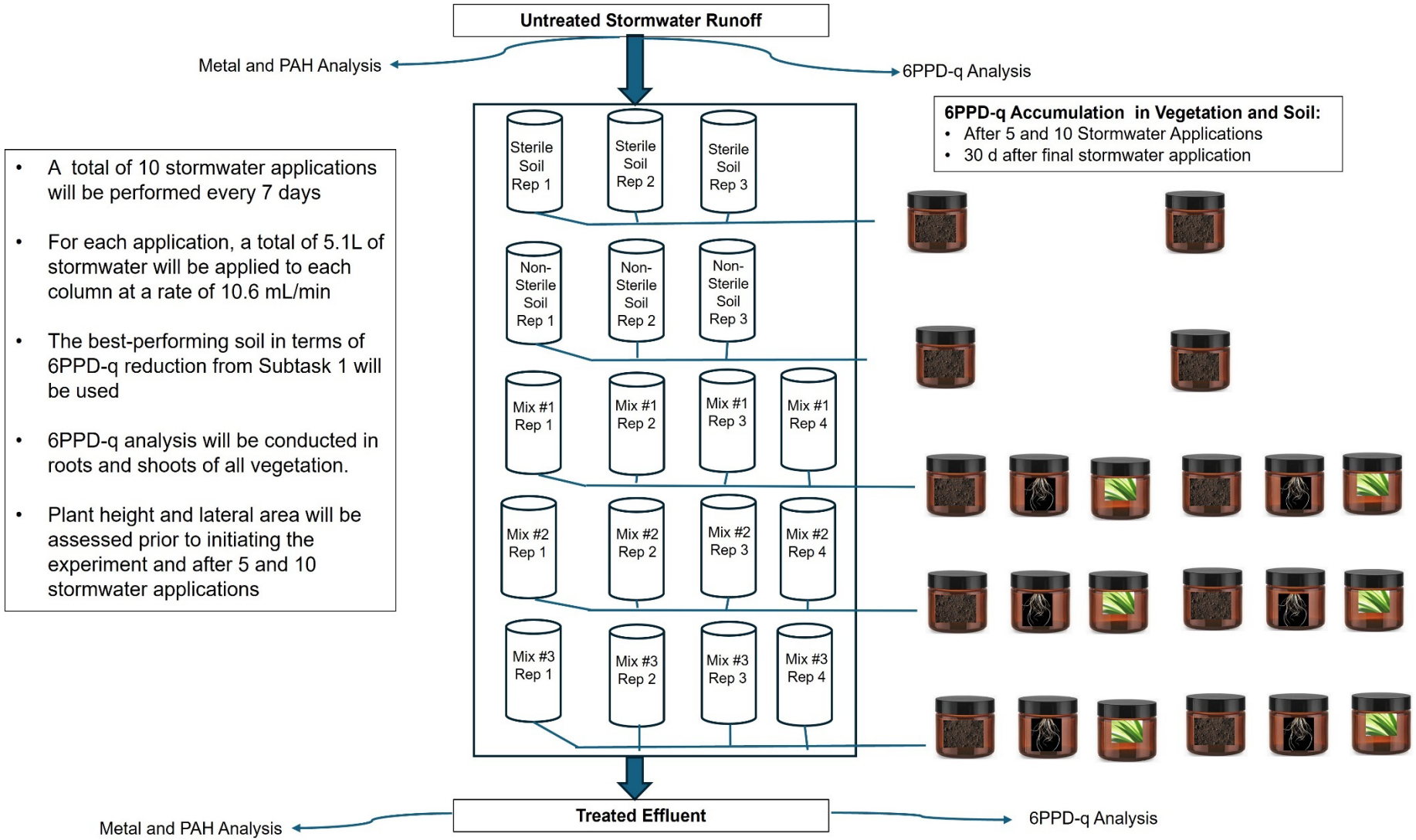

Figure 3. Schematic for the Soil-Vegetation Column Testing Study (Task 5).

Organization and Schedule

This project will be performed with collaboration between EA's Seattle office and the Ecotoxicology facility in Hunt Valley, MD.

Key individuals and responsibilities

The table below summarizes the key staff involved in the project and their individual responsibilities.

Table 7. Key Project Staff and Responsibilities.

Title	Name and Contact Information	Affiliation	Responsibilities
Ecology Project Manager	Madison Rose Bristol (564) 669-4582	Ecology	Assists with scope and goals of the project, provides internal review of all project deliverables and final approval.
Ecology WQ QA Coordinator	Chris Dudenhoeffer (360) 870-8409	Ecology	Reviews and approves draft and final QAPP.
Ecology 6PPD Stormwater Engineer	Shelby Giltner (360) 746-9182	Ecology	Technical reviewer of all project deliverables.
EA Project Manager	Richard Price (206)452-546	EA Seattle	Responsible for project execution, reporting, and invoicing. Oversees QAPP and deliverable development, contact person for Ecology.
EA Technical Lead	Jamie Suski (410)527-2459	EA Hunt Valley	Drafts QAPP and deliverables, coordinates logistics with the laboratory manager, interprets study results and drafts reports for Ecology
EA Laboratory Manager	Michael Chanov (410)329-5120	EA Hunt Valley	Responsible for overseeing all laboratory bioretention columns and management of laboratory staff. Constructs bioretention columns, provides updates on lab studies to Ecology.

Title	Name and Contact Information	Affiliation	Responsibilities
EA Senior Scientist	Neil Fuller (618)799-9245	EA Hunt Valley	Assists in developing QAPP, deliverables, and analysis of all data from the project. Liaises with field and laboratory staff to assist in project oversight.
EA Field Lead	Drew Roberts (206)452-5344	EA Seattle	Responsible for overseeing field collection and shipment of soils and stormwater from Washington.
6PPD Analysis Lead	Todd Anderson (806)834-1587	Texas Tech University	Manages and oversees analysis of 6PPD and 6PPDQ in all matrices (stormwater, soil, and vegetation). Provides reports of chemical analysis to EA.
Laboratory Director	Matt Langston	Alliance Technical Group, LLC.	Manages and oversees analysis of metals and PAHs in all matrices (stormwater, soil, and vegetation). Provides reports of chemical analysis to EA.

Special training and certifications

The field lead, Drew Roberts, is a certified natural resource professional and a State of Washington Certified Erosion & Sediment Control Lead. The proposed field team has experience and training in collection of stormwater samples for contaminant analyses, as well as soil collection methods and minimizing cross-contamination of samples and sampling equipment.

The toxicology lab where bioretention column studies will be performed is certified under the National Environmental Laboratory Accreditation Program. Staff performing the laboratory studies are trained in procedures including sample collection, chain of custody procedures for shipping and receiving samples, and handling environmental samples to minimize potential contamination.

Proposed project schedule

Project schedule

An overall project schedule is required as well as a detailed breakdown for each storm cycle and application.

Table 8. Project Schedule by Task

Task	Target Date
QAPP Complete and Approved by Ecology	October 10, 2024
Bioretention Columns Constructed	October 31, 2024
Soils Collected for Bioretention Columns	November 6, 2024
Bioretention Columns Filled and Ready for Experiments, Vegetation Planted for Task 5.	November 15, 2024
Weekly Stormwater Sampling and Task 4 Begins	November 20, 2024
Stormwater Applications Complete, Soil Persistence Begins	December 18, 2024
Soil Persistence Studies End	April 17, 2025
Weekly Stormwater Sampling and Application to Soil-Vegetation Systems for Task 5	February 10, 2025
Completion of Task 5	May 14, 2025
Data Analysis, Report Writing Completion	June 30, 2025

Schedule for stormwater collections

Schedule constraints for the collection of stormwater are as follows:

- Day of the week. Stormwater collections will be targeted for Monday through Wednesday to allow for shipping time to Hunt Valley, Maryland. In addition, stormwater collections will be performed preferentially in the morning to allow for time for shipment drop off.
- Antecedent dry period. The number of days with dry weather, defined as 0 – 0.13 cm of rain, prior to a sampled storm should be 0 – 2 days. This is to reduce the volume of suspended material in collected stormwater that may clog bioretention columns.

An approximate schedule for stormwater collection is given below:

Day 1

- Collect stormwater sample from Lake Union Ship Canal
- Send subsamples of stormwater to TTU and the contract laboratory for 6PPDQ and metal/PAH analysis, respectively.
- Ship carboys of stormwater to EA's Ecotoxicology laboratory for use in columns

Day 2

- Receive stormwater at EA's Ecotoxicology laboratory, document condition and water quality parameters, add to equilibration tanks for mixing.

Day 3

- Apply collected stormwater to bioretention columns.

During the period between stormwater cycles, collection equipment will be decontaminated using acetonitrile as described in Draft EPA Method 1634 (EPA 2024).

Potential schedule constraints

Climatic conditions, such as insufficient rainfall or extreme weather, have the potential to impact the proposed schedule by delaying collection of stormwater samples. In addition, staff availability, equipment malfunctions, and delays to funding sources have the potential to constrain the proposed schedule.

Budget and Funding

The funding source for the study is Ecology through the Environmental Consulting Services statewide contract. Payment requests will be sent to Ecology including a description of the work performed, progress, and related costs. The total project cost is $320,273. A budget by task is provided in Table 9.

Table 9. Budget for the project disaggregated by item and task.

Tasks Associated	Item	Amount
All	Project Management	$6,549
1	QAPP Writing and Revision	$10,304
2	EA Toxicology Lab – Staff & Bioretention Column Supplies Cost	$63,062
3	Field Soil and Stormwater Collections	$ 26,352
4 and 5	6PPD-q Analyses in Stormwater, Vegetation, and Soil	$100,625
4 and 5	Metal Analyses in Stormwater/Soil	$34,767
4 and 5	PAH Analysis in Stormwater/Soil	$33,906
4 and 5	Soil Characteristic Analyses	$5,628
5	Soil Microbial Analyses	$2,000
4, 5, and 6	Laboratory & Chemical Analysis	$239,988
7	Economic Analysis	$17,600
7	Communications	$19,480
	Total Project Cost	**$320,273**

Quality Objectives

Data quality objectives (DQOs) are both qualitative and quantitative statements that define the type, quality, and quantity of data necessary to support the defined project activities. The overall objective is to establish standard procedures so that the integrity, accuracy, precision, completeness, and representativeness of collected samples are maintained, and the required DQOs are achieved. The DQOs provided here follow the EPA's seven step process (EPA 2006) as follows:

1. State the problem
2. Identify the goals of the study; state the decisions to be made to solve the problem.
3. Identify information inputs; identify information and supporting measurements needed to take the decisions and describe the source(s) of the information.
4. Define the boundaries of the study; specify conditions (i.e., time periods and spatial locations).
5. Develop the analytic approach.
6. Specify performance or acceptance criteria.
7. Develop the plan for obtaining data; evaluate the results of the previous steps and develop the most resource-efficient design for data collection.

The DQOs following this process are provided below.

Data quality objectives

Step 1: State the problem

At present, the use of unamended soils as a LID BMP for stormwater mitigation is limited by a lack of data regarding these soils contaminant reduction capacity, with studies to date focusing on BSM. Furthermore, the persistence of 6PPD and 6PPDQ in unamended soils following their implementation in bioretention systems has not been determined. In addition, the efficacy of different soil-vegetation mixes and microbial communities in reducing 6PPD and 6PPDQ contamination has not been empirically studied with column experiments.

Step 2: Identify the Goal of the Study

The goals of the study are as follows:

1. Determine the reduction capacity of three unamended soils varying in characteristics including infiltration rate, CEC, and organic matter content
2. Elucidate the persistence of stormwater contaminants in unamended soil after use in bioretention columns
3. Identify the potential of soil-vegetation mixes to enhance reduction of stormwater contaminants in bioretention systems

4. Characterize the potential of other stormwater contaminants such as metals and PAHs to be used as proxies for 6PPDQ contamination.

Step 3: Identify the Information Inputs

The following data are needed to achieve the project goals:

- Soil characteristic data including percent organic carbon, CEC, infiltration rate, pH, and particle size.
- Chemical data (6PPDQ, metals, and PAHs) for stormwater, unamended soils, and vegetation
- Microbial community data for soil with 16s RNA analysis

Step 4: Define the Boundaries of the Study

This step can be subdivided into spatial and temporal boundaries. In terms of spatial boundaries, all field collections of stormwater will be conducted at the Lake Union Ship Canal Test Facility, located close to the I-5 bridge in Lake Union, Seattle. Exact spatial boundaries for soil collection will be determined with local field sampling teams based on availability of soil from areas with low urban associated land use. All column experiments will be performed at EA's Ecotoxicology Laboratory in Hunt Valley, Maryland.

For temporal boundaries, initial soil sampling is anticipated to occur in September/October 2024, with stormwater collections beginning early fall and continuing as required. Project completion is estimated by July/August 2025.

Step 5: Develop the Project Data Collection and Analysis Approach

Analysis of contaminant data in stormwater, soils, and soil-vegetation mixes will be used to address the goals identified in Step 2. The approach to data collection and analysis is documented in detail elsewhere within the QAPP. Data collection activities planned for this project are listed below.

Soil Sampling:

- Soil characteristic analysis will be used to determine the influence of soil parameters on contaminant reduction capacity.
- Analysis of contaminant concentrations in soil after use for bioretention will be used to determine the potential persistence of stormwater contaminants.
- Microbial community analysis will be used to elucidate the bacterial diversity and functional groups of microbes present in soil.

Stormwater Sampling:

- Stormwater contaminant analysis will be used to determine the concentrations of 6PPDQ, metals, PAHs, and potential associations among these contaminants

Effluent Sampling:

Contaminant analysis will be used to determine the reduction capacity of unamended soils and soil-vegetation systems.

Vegetation Sampling

- Contaminant analysis of different vegetation components (roots and shoots) will facilitate an understanding of stormwater contaminant uptake in soil-vegetation systems.

Step 6: Specify Performance or Acceptance Criteria.

The data obtained needs to be of sufficient quality to meet the project goals outlined above in Step 1. Consequently, data quality indicators were developed and are presented in the following section.

Step 7: Develop the Detailed Plan for Obtaining Data

The overall approach to data collection is discussed in the Laboratory and Field Procedures sections of this QAPP.

Data quality indicators

Indicators for accuracy, bias, completeness, precision, and sensitivity

This section describes the DQIs that form the basis of assessing data quality and usability. An overall summary of DQIs is given in Table 10, with a detailed list by individual analysis in Tables 11 to 13. This experiment does not have specific regulatory standards determining analytical requirements. As such, DQIs are based on the capacity of the analytical laboratories involved in the project and requirements of their internal protocols. Definitions of the individual DQI components are provided below:

Precision – A measure of the repeatability of a set of replicated results conducted under the same or similar conditions. To ensure analytical precision, relative percent difference (RPD) of laboratory duplicate samples can be calculated according to the following equation:

$$\text{RPD} = \frac{X_1 - X_2}{\frac{X_1 + X_2}{2}} * 100$$

Where X¬1 and X2 represent the original and duplicate sample concentrations, respectively. For this project, bioretention columns will be examined in triplicate to increase precision of the obtained measurements.

Accuracy and Bias – Accuracy is defined as the extent of the agreement between an observed value and the actual value of the parameter being measured. Within the analytical procedure, accuracy can be assessed using matrix spike (MS) and matrix spike duplicate (MSD) samples, within which a known concentration of an analyte of interest has been added. Percent recovery of the analyte of interest is defined using the equation below and used as one measure of analytical accuracy.

$$\%\, recovery = \frac{C_{Measured}}{C_{True}} * 100$$

Where $C_{Measured}$ and C_{True} represent the measured and true value of a given analyte, respectively

Bias can be defined as 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.

Instrument calibration and quality control (QC) samples, such as field blanks, laboratory blanks, and matrix spikes, can be used to assess the accuracy and bias of field and laboratory measurements. Field blanks will be included when collecting stormwater samples to determine potential bias associated with field procedures. Similarly, laboratory blanks will be incorporated into all contaminant analyses to determine the potential introduction of contamination within the analytical procedure.

Completeness – Completeness is defined as the number of valid measurements relative to the total number of planned measurements. The following equation can be used to determine the percentage of complete values:

$$Completeness = \frac{Number\ of\ Valid\ Results}{Number\ of\ Samples\ Tested} * 100$$

Sensitivity – Sensitivity is the ability of the method or instrument to detect the value at the level of interest. Sensitivity will be determined by the quality of the instruments/equipment used and by the specific calibration methods. Specific method detection limit (MDL) and reporting limits (RLs) for the analyses of interest are listed in Tables 11 to 13.

Table 10. Summary of Data Quality Indicators for All Analyses

Analysis	Analytical Method	Data Quality Indicators	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance
6PPDQ	EPA Method 1634 (Water), QuECHERs and EPA Method 1634 (Soil and Vegetation)	Precision	RPD < 20% (Stormwater) RPD < 50% (Soil and Vegetation)	Field Duplicate
		Accuracy/Bias/Precision	70-130%; RPD ≤30%	Laboratory Control Sample (LCS) and Matrix Spike/Matrix Spike Duplicates (MS/MSD)
		Accuracy/Laboratory Contamination	No analytes detected above the method reporting limit (RL)	Laboratory Blank (LB)
		Accuracy/Field Contamination	No analytes detected above the method reporting limit (RL)	Field Blank
		Completeness	>95%	Reported Sample Data
		Bias/Holding Time	≤14 days to extraction, ≤28 days to analysis	Reported Sample Data
		Sensitivity	Table 11	Detection limits
Metals	EPA Method 6020B	Precision	Relative percent difference (RPD) ≤ 20%	Field Duplicate
		Accuracy/Bias/Precision	70-130%; RPD ≤20%	Laboratory Control Sample (LCS) and Matrix Spike/Matrix Spike Duplicates (MS/MSD)
		Bias/Holding Time	≤ 6 months to extraction and analysis,	Reported Sample Data
		Sensitivity	Table 12	Detection limits

Analysis	Analytical Method	Data Quality Indicators	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance
PAHs	EPA Method 8270E	Precision	Relative percent difference (RPD) ≤ 30%	Field Duplicate
		Accuracy/Bias/Precision	40 – 140%; RPD ≤20%	Laboratory Control Sample (LCS) and Matrix Spike/Matrix Spike Duplicates (MS/MSD)
		Bias/Holding Time	≤14 days to extraction, ≤28 days to analysis	Reported Sample Data
		Sensitivity	Table 13	Detection limits
Soil Organic Matter	ASTM D2974 or EPA 9060A	Precision	Relative percent difference (RPD) ≤ 20%	Field Duplicate
		Bias/Holding Time	≤28 days to analysis	Reported Sample Data
		Sensitivity	0.1%	Detection Limits
Soil CEC	EPA Method 9081	Precision	Relative percent difference (RPD) ≤ 20%	Field Duplicate
		Bias/Holding Time	≤28 days to analysis	Reported Sample Data
		Sensitivity	0.003 meq/100g	Detection Limits
Soil Grain Size	ASTM Method D422	Precision	N/A	N/A
		Bias/Holding Time	N/A	N/A
		Sensitivity	N/A	N/A

RPD = Relative Percent Difference
LB = Laboratory Blank
MS = Matrix Spike
MSD = Matrix Spike Duplicate
QC = Quality Control
meq = milliequivalents
N/A = Not Applicable

Table 11. Data Quality Indicators for Analysis of 6PPDQ in Stormwater, Soil, and Vegetation

Compound	Method	Matrix	Units	MDL	RL	Lab Blank	Laboratory Duplicate RPD	LCS and MS Recovery (%)
6PPDQ	1634	Stormwater	ng/L	0.5	2.0	< RL	< 20	70 - 130
6PPDQ	1634	Soil	µg/kg	0.073	0.250	< RL	< 50	70 – 130
6PPDQ	1634	Vegetation	mg/kg	0.073	0.250	< RL	< 50	70 – 130

RPD = Relative percent difference
RL = Reporting Limit
ng/L = nanograms per liter
µg/kg = micrograms per kilogram
mg/kg = milligrams per kilogram
MDL = Method Detection Limit
LCS = Laboratory Control Sample
MS = Matrix Spike

Table 12. Data Quality Indicators for Analysis of Metals in Soil and Stormwater

Compound	Method	Units	MDL	RL	Method Blank	Laboratory Duplicate RPD	LCS and MS Recovery (%)
Soil							
Cadmium	6020B	mg/kg	0.00581	0.02	< RL	< 20	75 - 125
Copper	6020B	mg/kg	0.691	2	< RL	< 20	75 - 125
Lead	6020B	mg/kg	0.0734	0.2	< RL	< 20	75 - 125
Mercury	6020B	mg/kg	0.00731	0.04	< RL	< 20	75 - 125
Zinc	6020B	mg/kg	2.00	15.0	< RL	< 20	75 - 125
Stormwater							
Cadmium	6020B	µg/L	0.0301	0.05	< RL	< 20	75 - 125
Copper	6020B	µg/L	0.868	2	< RL	< 20	75 - 125
Lead	6020B	µg/L	0.0796	0.300	< RL	< 20	75 - 125
Mercury	6020B	µg/L	0.0123	0.1	< RL	< 20	75 - 125
Zinc	6020B	µg/L	1.16	2.5	< RL	< 20	75 - 125

RL = Reporting Limit
µg/L = micrograms per liter
RPD = Relative percent difference
MDL = Method Detection Limit
mg/kg = milligrams per kilogram
LCS = Laboratory Control Sample
MS = Matrix Spike

Table 13. Data Quality Indicators for Analysis of PAHs in Soil and Stormwater

Compound	Method	Units	MDL	RL	Method Blank	Laboratory Duplicate RPD	LCS and MS Recovery (%)
Soil							
1-Methylnaphthalene	8270E	mg/kg	0.0031	0.02	< RL	< 30	40 - 130
2-Methylnaphthalene	8270E	mg/kg	0.0032	0.02	< RL	< 30	40 - 130
Acenaphthene	8270E	mg/kg	0.0023	0.02	< RL	< 30	40 - 130
Acenaphthylene	8270E	mg/kg	0.0029	0.02	< RL	< 30	40 - 130
Anthracene	8270E	mg/kg	0.0027	0.02	< RL	< 30	40 - 130
Benzo[a]anthracene	8270E	mg/kg	0.0071	0.02	< RL	< 30	40 - 130
Benzo[a]pyrene	8270E	mg/kg	0.0061	0.02	< RL	< 30	40 - 130
Benzo[b]fluoranthene	8270E	mg/kg	0.0058	0.02	< RL	< 30	40 - 130
Benzo[g,h,i]perylene	8270E	mg/kg	0.0091	0.04	< RL	< 30	40 - 130
Benzo[k]fluoranthene	8270E	mg/kg	0.0048	0.02	< RL	< 30	40 - 130
Chrysene	8270E	mg/kg	0.0033	0.02	< RL	< 30	40 - 130
Dibenz(a,h)anthracene	8270E	mg/kg	0.0072	0.02	< RL	< 30	40 - 130
Fluoranthene	8270E	mg/kg	0.0044	0.02	< RL	< 30	40 - 130
Fluorene	8270E	mg/kg	0.0024	0.02	< RL	< 30	40 - 130
Indeno[1,2,3-cd]pyrene	8270E	mg/kg	0.0079	0.02	< RL	< 30	40 - 130
Naphthalene	8270E	mg/kg	0.0028	0.02	< RL	< 30	40 - 130
Phenanthrene	8270E	mg/kg	0.0032	0.02	< RL	< 30	40 - 130
Pyrene	8270E	mg/kg	0.0068	0.02	< RL	< 30	40 - 130
Stormwater							
1-Methylnaphthalene	8270E	µg/L	0.0081	0.1	< RL	< 30	40 - 130
2-Methylnaphthalene	8270E	µg/L	0.017	0.1	< RL	< 30	40 - 130
Acenaphthene	8270E	µg/L	0.020	0.1	< RL	< 30	40 - 130
Acenaphthylene	8270E	µg/L	0.017	0.1	< RL	< 30	40 - 130
Anthracene	8270E	µg/L	0.015	0.1	< RL	< 30	40 - 130
Benzo[a]anthracene	8270E	µg/L	0.021	0.1	< RL	< 30	40 - 130
Benzo[a]pyrene	8270E	µg/L	0.020	0.1	< RL	< 30	40 - 130
Benzo[b]fluoranthene	8270E	µg/L	0.025	0.1	< RL	< 30	40 - 130
Benzo[g,h,i]perylene	8270E	µg/L	0.026	0.1	< RL	< 30	40 - 130
Benzo[k]fluoranthene	8270E	µg/L	0.010	0.1	< RL	< 30	40 - 130
Chrysene	8270E	µg/L	0.009	0.1	< RL	< 30	40 - 130
Dibenz(a,h)anthracene	8270E	µg/L	0.022	0.1	< RL	< 30	40 - 130
Fluoranthene	8270E	µg/L	0.020	0.1	< RL	< 30	40 - 130
Fluorene	8270E	µg/L	0.017	0.1	< RL	< 30	40 - 130
Indeno[1,2,3-cd]pyrene	8270E	µg/L	0.024	0.1	< RL	< 30	40 - 130

Compound	Method	Units	MDL	RL	Method Blank	Laboratory Duplicate RPD	LCS and MS Recovery (%)
Naphthalene	8270E	µg/L	0.021	0.1	< RL	< 30	40 - 130
Phenanthrene	8270E	µg/L	0.011	0.1	< RL	< 30	40 - 130
Pyrene	8270E	µg/L	0.016	0.1	< RL	< 30	40 - 130

RL = Reporting Limit
µg/L = micrograms per liter
RPD = Relative percent difference
MDL = Method Detection Limit
µg/kg = micrograms per kilogram
LCS = Laboratory Control Sample
MS = Matrix Spike.

Indicators for comparability and representativeness

In addition to the DQIs highlighted above, DQIs for comparability and representativeness are required to understand the extent to which the generated data can be applied in the wider context.

Comparability – Comparability is defined as the extent to which data obtained from this study can be compared directly to data from other studies. The analytical results for 6PPDQ, metals, and PAHs within stormwater collected from the Lake Union Ship Canal site can be compared to previous data from the site from previous research efforts. In addition, stormwater contaminant loads can be compared to other sites from Ecology's National Pollutant Discharge Elimination System (NPDES) and WSDOTs NDPES Municipal Stormwater Permit. Methodology for this experiment is broadly consistent with previous assessments using bioretention media conducted by McIntyre et al. (2015, 2023), facilitating a comparison between studies.

Representativeness – Representativeness is a qualitative assessment of the degree to which the sampling design adequately represents the environmental conditions of the chosen sampling site. The selected stormwater collection site drains a heavily used urban highway in the Puget Sound and has been used extensively in previous stormwater management studies. Furthermore, the use of stormwater collected from a total of 15 different storm events will aid in ensuring representativeness.

Field Procedures

This section will describe the field procedures used in collecting soils and stormwater for bioretention studies

Soil collections

The field lead and GIS specialists at EA's Seattle office will identify appropriate soil sampling locations based on the criteria described previously and the WA soil database from the Washington Geospatial Open Data Portal. The WA soil database contains information including the soil type (i.e., sandy loam, gravelly loam, sand), drainage capacity, and depth. To minimize the potential for background contamination with 6PPDQ and other stormwater contaminants, soil collection sites in heavily urbanized areas will be avoided where possible. Once appropriate sampling sites are located and confirmed with Ecology, a site visit and soil collections will be performed. A large quantity of soil will be required based on the number of bioretention columns and the depth of fill required.

Amount of soil required for task 4

To calculate the amount of soil required per soil type for Task 4, the following details are required:

- The number of replicate columns per soil type. Three replicate columns will be used per soil type for Task 4
- Volume of soil required for each bioretention column. Each column will be filled with soil to a depth of 45.7 cm (equivalent to 18 in). Therefore, the calculated soil volume of each cylinder is 8,293 cm^3 ($\pi * 7.6^2 * 45.7$), equivalent to 0.00829 m^3 or 0.0108 cubic yards.

Assuming a bulk soil density of ~ 1.33 g/cm^3 (USDA 2008), this would necessitate collection of a minimum of 11.0 kg per column for each soil type, with additional required to ensure adequate fill of bioretention columns and for preliminary soil characteristic/contaminant analyses. Accounting for the three replicate columns the total amount of each soil type required is $0.00829 * 3 = 0.0249$ m^3 by volume and $11.0 * 3 = 33.0$ kg by mass. Additional soil is required to perform background contaminant analysis and in case of loss; thus, an additional 15% will be collected, totaling 0.0286 m^3 by volume and 38.0 kg by mass for each soil type. The BSM designated for use in Task 4 will be purchased by the cubic yard from StormwaterBiochar.

Amount of soil required for task 5

Task 5 requires use of the best performing soil from Task 4 for use in soil-vegetation columns. A total of 18 columns containing the chosen soil will be used in this experiment. Based on the calculated soil volume of each column calculated in the preceding section, a total of 0.149 m^3 (0.195 cubic yards) or 198 kg of the chosen soil will be required, with an additional 15% totaling 0.171 m^3 or 228 kg.

Soil collection methods

After appropriate soil collection sites are located and confirmed with Ecology staff, EA's field team will perform a site visit at each of the target locations to determine if adequate soil is available. When an appropriate site is located, soil collection will be performed. Infiltration rate will be assessed in the field using the falling head method, with the *ex-situ* grain size analysis method used to provide confirmation of rates according to the 2024 SMMWW (Ecology 2024). The two other approved *in-situ* methods for determining the infiltration rate of soils in the SMMWW, the large- and small-scale pilot infiltration tests, involve excavation of a large area and are logistically challenging; thus, the falling head method will provide a rough estimate of field infiltration rates followed by the approved laboratory-based grain size method. The grain size method involves estimation of initial saturated hydraulic conductivity (K_{sat}) based on well-documented empirical relationships with grain size. The American Society for Testing and Materials (ASTM) soil size distribution test procedure, Method ASTM D422, is used to develop soil size distribution curves, followed by application of the below equation to calculate K_{sat}

$$log_{10}(K_{sat}) = -1.32 + 1.225 * d_{10} - 0.376 * f_{fines}$$

where:

K_{sat} = saturated hydraulic conductivity (cm/sec)
d_{10} = grain size for which 10% of the sample is finer (mm)
f_{fines} = fraction of the soil (by weight) that passes a No. 200 sieve

In terms of soil collections, the topsoil (0 – 15 cm below ground surface [bgs]) will be preferentially collected for each soil type to avoid differences in soil characteristics with soil depth. Soils will be collected using a stainless-steel corer and transferred to 26.5 L buckets (equivalent to 7 gallons) with a capacity of 0.0275 m^3 for shipment to EA's Ecotoxicology laboratory. In addition, homogenized subsamples of soil will be taken for 6PPDQ, metal, PAH, and soil characteristic analysis. Specific containers, preservatives, and hold times are given in Table 14.

Stormwater collections

The stormwater collection location is the Lake Union Ship Canal Test Facility shown below in Figure 4. To identify appropriate storm events for sampling, the EA Seattle field team will monitor weather forecasts weekly during the project period. The following criteria will be used to determine whether a storm is suitable for sampling:

- At least 0.6 cm (0.25 in) of rain forecast over a 12-hour period
- Antecedent dry period (defined as < 0.13 cm of rain) of 1 to 2 days is preferred
- Adequate field staff availability for stormwater sampling and shipping
- The storm occurs on Monday, Tuesday, or Wednesday to allow time for shipping of stormwater to Maryland

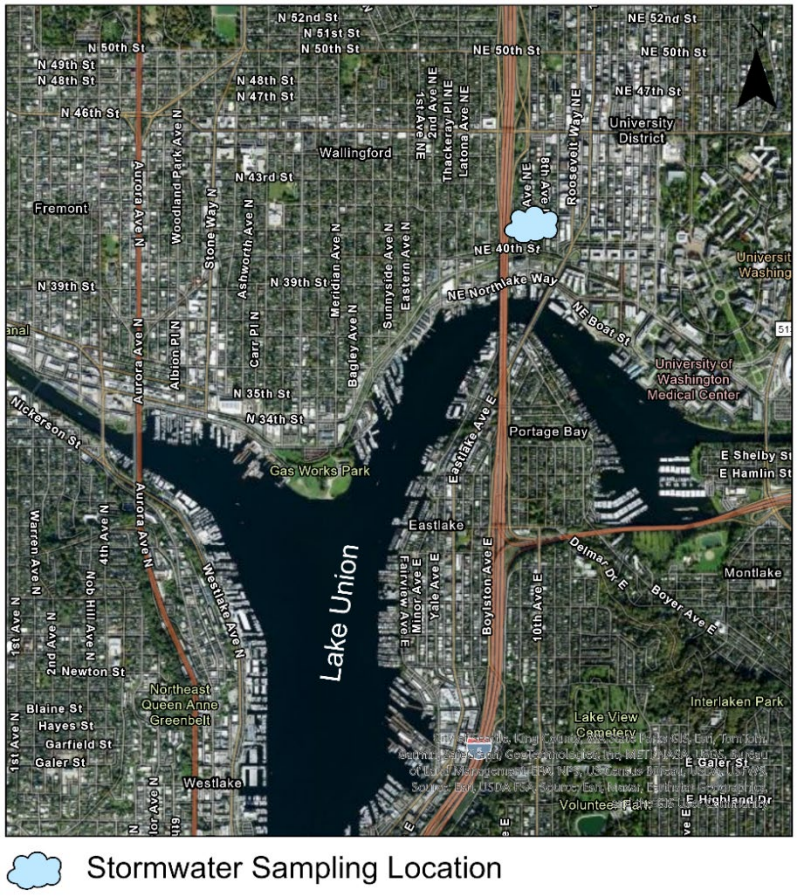

Figure 4. Location of the Stormwater Sampling Site.

At the collection site, stormwater flows through a network of polyvinyl chloride (PVC) pipes with various access locations. All stormwater samples will be collected by opening a supply valve with dedicated tubing leading to an 9.5 L HDPE carboy (equivalent to 2.5 gallons). Collection methods will broadly follow Ecology's SOP for stormwater collection (Appendix B). The amount of stormwater required for each storm event is 61.2 L for Task 4 and 91.8 L for Task 5; thus, 7 carboys will be required for each storm event for Task 4, and 10 for Task 5. A smaller capacity carboy was chosen preferentially since this size fits within coolers that can be filled with ice. A total of five and ten storm events are planned for Task 4 and 5, respectively. At each storm event, subsamples of stormwater will be collected for 6PPDQ, metal, and PAH analysis. The sample containers for these subsamples are given in Table 14.

After each stormwater collection event, 9.5 L carboys will be placed into insulated coolers with wet ice for shipment to the Ecotoxicology laboratory. Subsamples of stormwater will be packaged and shipped to analytical laboratories dependent on the specific analysis. All samples designated for 6PPDQ analysis will be TTU's Department of Environmental Toxicology. Rationale for the use of TTU for 6PPDQ analyses is provided in the Laboratory Procedures section below. Samples designated for metal and PAH analysis will be shipped to the designated contract

laboratory. Further details on the sample containers, preservatives, and hold times are given in Table 14.

Table 14. Sample Containers, Preservatives, and Hold Times for Soil and Water.

Matrix	Analysis/Use	Container	Preservative	Hold Time
Stormwater	Bioretention Studies	9.5 L HDPE carboy	4 °C ice, minimize head space	Ship to Hunt Valley same day
Stormwater	6PPDQ	250 mL amber glass jar, PTFE-lined cap	4 °C ice, minimize head space, do not freeze.	14 days
Stormwater	Metals	250 mL HDPE bottle	HNO_3 upon receipt	6 months
Stormwater	PAHs	500 mL amber glass jar	4°C ice	7 days
Bulk Soil	Bioretention Studies	26.5 L Bucket	None	Ship to Hunt Valley within 7 d
Soil	6PPDQ analysis	250 mL amber glass jar, PTFE-lined cap	4 °C ice, minimize head space, do not freeze.	14 days
Soil	Metals	236 mL glass	4 °C ice	180 days
Soil	PAHs	236 mL glass	4 °C ice	14 days
Soil	OC, pH, CEC, and Particle Size	236 mL glass, 473 mL glass for particle size.	4 °C ice	Various
Vegetation	6PPDQ analysis	Polyethylene Bags	4 °C ice	No guidance.

Equipment decontamination

Equipment used for all sample collections including soil corers, carboys, and other tools will be decontaminated using an initial acetonitrile rinse followed by washing with Liquinox® liquid detergent and deionized water.

Sample identification

For soil samples, all containers will be labelled with the following details:

- Collection location/bioretention column ID
- Time and date of collection (24-hour format, year/month/day)
- Initials of sampling personnel
- Analyses required

For stormwater samples, containers will be labelled with the following details:

- Sample type (i.e., untreated stormwater or bioretention column effluent)
- Collection location/bioretention column ID

- Time and date of collection (24-hour format, year/month/day)
- Initials of sampling personnel
- Analyses required

For the vegetation samples, containers will be labelled with the following details:

- Sample type (i.e., root/shoot/leaves)
- Bioretention column ID
- Time and date of collection (24-hour format, year/month/day)
- Initials of sampling personnel
- Analyses required

Chain of custody

Chain of custody (COC) forms will be provided by the contract analytical laboratory for all metal, PAH, and soil characteristic analysis. For sample transfer between EA's Seattle and Hunt Valley offices and samples for 6PPDQ analysis, custom COC forms containing the following details will be used: Sample ID, matrix type (i.e., stormwater, soil, or vegetation), analysis required, sample date and time, number of containers included, container type, preservative, signature of relinquishing personnel, and date/time of relinquishment. All sample shipments will include a copy of the COC inside a Ziploc bag as well as an electronic copy. Upon receipt of samples, receiving personnel will sign the COC forms and provide a copy to EA staff for filing. Examples of COC forms are provided in Appendix A.

Field log requirements

Field logs will be maintained during all field activities including soil and stormwater collections. The following details will be included for soil collection field logs:

- Time and date of sampling activities (24-hour format, year/month/day)
- Field personnel performing sampling
- Sample location (site name and GPS coordinates)
- Weather conditions including ambient temperature
- Approximate volume of soil sampled and number of containers
- Labelling details for containers
- Sample handling and transport

For stormwater collections, the following details will be included on field logs:

- Time and date of sampling activities (24-hour format, year/month/day)
- Field personnel performing sampling
- Sample location
- Weather conditions and amount of precipitation in storm event
- Number of carboys and subsamples collected
- Labelling details for containers
- Sample handling and transport
- Any deviations from standard methods or the QAPP

Example field sheets are provided in Appendix A. Details for logs taken during bioretention column studies will be provided in the following section.

Laboratory Procedures

This section describes laboratory procedures for performing column studies as well as analytical methods for analysis of 6PPDQ, metals, PAHs, and soil characteristics.

Bioretention column studies

A detailed description of the methods proposed and experimental design for laboratory bioretention studies is provided in the Experimental Processes and Tasks section above.

6PPDQ analytical methods

All 6PPDQ analyses will be performed at TTU's Department of Environmental Toxicology. This lab was selected to conduct exclusively exploratory (not regulatory) research, to analyze multiple matrices for 6PPDQ, including tissues, sediment, and water samples, and to reduce overall project financial and carbon costs. First, EA has a successful history of collaborating with TTU on 6PPDQ projects including analyses of soil, sediment, and surface water from various Department of Defense sites. From this collaboration, recoveries for all matrices met criteria proposed in EPA's Draft Method 1634, including average recoveries of 79.3% ± 2.5% and 77.8% ± 4.9% for 6PPDQ and C^{13} 6PPDQ, respectively in surface water samples, with recovery limits of 70 – 130% proposed by EPA (EPA 2024). Similarly, recovery of 6PPDQ and C^{13} 6PPDQ was 105% ± 12% and 122% ± 11%, respectively in soil/sediment matrices thus meeting the aforementioned recovery criteria. Importantly, no specific method for solids has been published to date. Within these analyses, method reporting limits of 2 ng/L and 0.15 ng/g for surface water and solids, respectively were achieved in line with the minimum quantification level of 2 ng/L proposed by EPA in Draft Method 1634. These findings demonstrate adherence to method performance criteria at TTU and appropriate extraction and analysis techniques.

At present, no contract, state, or federal laboratories to our knowledge are offering analysis of 6PPDQ in tissue, necessitating the use of an alternative laboratory such as TTU for analysis of 6PPDQ in plant tissue. Furthermore, collaboration with TTU faculty provides a state-of-the-art academic laboratory and a rich history of analytical capabilities in emerging contaminants. Specifically, Dr. Anderson has over 22,500 citations of his extensive publication record and has demonstrated the expertise required for this research project. As such, performing all analyses at TTU rather than using multiple laboratories for 6PPDQ in different matrices offers a considerable advantage in terms of data comparability, consistency of methods, and logistics associated with sample shipping and transfer.

Additionally, the budget and costs for this project were developed contingent on the price estimate provided by TTU. Consequently, using TTU for 6PPDQ analyses will facilitate testing of a greater number of samples and a more robust overall assessment of the efficacy of unamended soils and different vegetation mixes on 6PPDQ removal. If use of another analytical laboratory is required, the project would have to be scaled down significantly to accommodate

the loss of collaboration and higher costs, likely resulting in fewer soil types, all vegetation mixes, and replicates tested, which will reduce the applicability and statistical power of the project.

It is important to consider that this is a lab-based, exploratory study, with data arising from this project not to be incorporated into regulatory decision-making. Knowledge gained from this project will help inform future laboratory and field research incorporating unamended soils into bioretention systems. Only after rigorous testing and application of an accredited lab for 6PPDQ analysis would data from future studies be used for regulatory purposes.

Stormwater

Methods for 6PPDQ analysis will follow Tian et al. (2022), Helm et al. (2024), and the draft EPA Method 1634 (EPA 2024). Briefly, water samples (100 mL) will be spiked with $^{13}C_6$-6PPDQ (extracted internal standard, EIS) and extracted using C18 solid phase extraction (SPE). 6PPDQ is eluted from the cartridge with acetonitrile, evaporated to dryness, then reconstituted to 250 µL final volume. The extract (SPE eluent) is spiked with D_5-6PPDQ (non-extracted internal standard, NIS) prior to analysis. Analysis will be conducted using liquid chromatography tandem mass spectrometry (LC-MS/MS).

Soil and vegetation samples

Dried soil samples will be spiked with $^{13}C_6$-6PPDQ (EIS) and extracted using a Quick Easy Cheap Effective Rugged Safe (QuEChERS)-based method and LC-MS water and LC-MS acetonitrile developed at TTU. Vegetation samples will be air-dried, spiked with $^{13}C_6$-6PPDQ (EIS), then extracted using a QuEChERS-based method our laboratory has used successfully with other analytes (Lasee et al. 2021). Filtered extracts of soil and vegetation samples will be analyzed using LC-MS/MS similar to EPA Method 1634 (EPA 2024).

Metal analytical methods

Analysis of metals in stormwater and soil will follow EPA Method 6020B, which measures trace elements at the parts per billion level in aqueous and solid samples (EPA 2014). Solid and aqueous samples are first acid digested and analyzed using Inductively Coupled Plasma-Mass Spectrometry. Analysis will be performed by an Ecology-accredited lab such as Edge Analytical Inc or Freemont Analytical Services.

PAH analytical methods

Analysis of PAHs in stormwater and soil will follow EPA Methods 3550C and 8270E for extraction and measurement, respectively. EPA Method 8270E measures semivolatile organic compounds using gas chromatography/mass spectrometry (GC/MS, EPA 2018). Sample preparation methods for aqueous samples typically involve liquid-liquid extraction, with Soxhlet or SPE commonly used for solid samples. Following sample preparation and any cleanup steps, extracts are analyzed using GC/MS.

Soil characteristic analyses

The following soil characteristics will be analyzed in the present study: total organic carbon, particle size, CEC, infiltration rate, and pH. The organic matter content of soils will be determined using ASTM method D2974 or EPA 9060A. Particle size will be determined using American Society for Testing and Materials (ASTM) Method D422 (ASTM 2014), which uses sieve analysis to characterize soil particles by their size distribution. CEC will be determined using EPA Method 9081 (EPA 1986), which involves addition of sodium acetate and ammonium acetate to soil followed by atomic adsorption or emission spectroscopy. Finally, soil pH will be determined using EPA Method 9045D (EPA 2004), which uses an electrometric procedure to measure pH in soils and waste with < 20% water.

Microbial community analysis

Soil microbial community analysis will be conducted using 16s rRNA methods at a contract laboratory. This method can be used to elucidate the abundance of microbial taxa and different functional groups within the soil microbiome. Briefly, DNA is extracted from samples using a commercially available kit such as Qiagen MagAttract PowerSoil (Qiagen, Germantown, MD) and the DNA quality is assessed using a fluorometric method such as Qubit. Following DNA extraction, polymerase chain reaction amplifications targeting bacteria 16S rRNA are performed. A bioinformatics pipeline such as Mothur or DADA2 will be used to analyze obtain data and provide an assessment of soil microbial diversity.

Quality Control Procedures

A number of quality control (QC) procedures will be implemented throughout both the laboratory and field components of this project. A summary table detailing all quality control procedures is listed in Table 15.

Table 15. Summary of all quality control procedures.

Quality Control Item	Matrix	Analysis	Frequency
Field Blank	Stormwater	6PPDQ, Metals, PAHs.	One per collection event
Replicates	Soil, Stormwater	6PPDQ, Metals, PAHs.	Three and four per study for Task 4 and 5, respectively
Replicates	Vegetation	6PPDQ, Metals, PAHs	Four per study
Laboratory Blanks		6PPDQ, Metals, PAHs.	One per analytical batch
Matrix Spike and Matrix Spike Duplicate	Soil, Stormwater	6PPDQ, Metals, PAHs.	One MS and MSD per analytical batch
Laboratory Duplicate	Soil, Stormwater	6PPDQ, Metals, PAHs.	One per analytical batch
Laboratory Control Samples	Soil, Stormwater, Vegetation	6PPDQ, Metals, PAHs	One per analytical batch

Replicates

For Task 4 bioretention columns will be analyzed in triplicate (i.e., three controls, three of each soil type for Task 4). Consequently, filtered effluent passed through bioretention columns and soil will be analyzed for 6PPDQ and other stormwater contaminants in triplicate during Task 4. Similarly, Task 5 will utilize four replicate columns within each treatment group; thus, filtered effluent, vegetation (roots and shoots), and soils will be analyzed in a total of four sample. Collected stormwater used for all column experiments (Tasks 4 and 5) will be analyzed in duplicate to minimize analytical costs while providing some degree of replication. Similarly, collected bulk soils designated for use in bioretention columns will be analyzed in singular for soil characteristics and background contamination with 6PPDQ and stormwater pollutants.

Laboratory and field blanks

For each stormwater collection event, a sample drawn from a carboy containing deionized water will represent a field blank to determine the potential for residual contamination associated with field practices and equipment. Prior to addition of stormwater to bioretention columns for Tasks 4 and 5, a sample of filtered effluent will be collected following addition of deionized water only to columns. This sample will be analyzed for all targeted contaminants (6PPDQ, metals, and PAHs) and will provide information on potential contamination associated with laboratory procedures and equipment.

Analytical laboratories conducting contaminant analyses will incorporate laboratory blanks in their methodology. These samples contain little or none of the analytes of interest and aid in determining potential sources of contamination associated with laboratory extraction procedures. Results for laboratory blank standards will be compared to project-specific MPCs and established acceptance criteria to determine if corrective action is required.

Corrective action

Deficiencies requiring potential corrective action include, but are not limited to, the following:

- Exceedances of holding time requirements
- Use of inappropriate sample containers
- Failure to calibrate instruments to appropriate protocols
- Failure to collect and/or analyze appropriate blanks and QC samples.

For deficiencies relating to chemical analyses, the analytical laboratory managers will be responsible for implementing corrective actions that may include reanalysis of samples, collection of additional samples if feasible, retrieval of missing information, and modification of sampling and analytical methods. The field team will be responsible for collection of any additional samples to address deficiencies.

Analytical standards

In addition to laboratory blanks, analytical laboratories will incorporate a range of QC samples including laboratory duplicates, check standards, and matrix spikes/matrix spike duplicates. For laboratory duplicates, received samples are split into two and analyzed separately to determine precision by comparing concentrations and relative percent difference (RPD) values. Check standards are samples of a known concentration prepared independently of the calibration standards. These samples are used to check precision and levels of bias, with raw concentration values and percent recovery included in all data reports. Finally, matrix spike (MS) and matrix spike duplicate (MSD) samples are used by the laboratory to indicate bias, and any method interference associated with the specific matrix tested (i.e., soil, vegetation or stormwater). Values for MS/MSD samples will be included with all data reports and compared to MPCs and method-specific acceptability criteria.

Data Management Plan and Procedures

Overall, data associated with this project will be generated by EA's Ecotoxicology laboratory (Hunt Valley), EA's Seattle Office, Texas Tech University, and an analytical contract laboratory. The data generated by EA will include field logs of soil and stormwater collections, soil infiltration rates determined in the field, and all non-contaminant data associated with column studies, including vegetation growth rates. Texas Tech University will generate 6PPDQ data for all matrices (soil, stormwater, and vegetation), with the contract laboratory generating all metal, PAH, and soil characteristic data. This section of the QAPP describes data management procedures for all project-associated data.

Data recording and reporting requirements

All observational data from field stormwater and soil collections will be recorded in a field logbook. Field logs and any additional notes will be transferred to an Excel spreadsheet within 5 days of field activities and paper logs field and stored. For the laboratory studies, all notes and data associated with column studies will be recorded within a laboratory notebook and

transferred to Excel within 5 days. Excel spreadsheets containing laboratory and field data will be cross-checked by another project researcher to determine accuracy.

Laboratory data package requirements

TTU and contract analytical laboratories will provide chemistry data to EA's project staff in an electronic form when analyses have been completed. Electronic data packages will include the following components:

- Case narrative describing any issues associated with the analyses
- Any corrective actions taken or deviations from standard methods
- QC results for laboratory blanks, duplicates, and MS/MSD samples
- A list describing any laboratory qualifiers
- Raw chemical data for all samples

Data storage procedures

Throughout the experiment, all data will be stored on EA's SharePoint in a dedicated directory. Data will be accessible to all project staff at the Ecotoxicology laboratory and EA's Seattle Office. Received analytical chemistry data from TTU and contract laboratories will be stored within a dedicated folder within this directory. Data will be shared with Ecology staff upon completion of the project and can be added to data repositories as required.

Audits and Reports

Audits

There are no audits planned for this project; however, audits of EA's Ecotoxicology laboratory may be performed by Ecology at its discretion. Analytical laboratories associated with this project undergo performance and system audits of their routine procedures.

Frequency and Distribution of Reports

The EA project team will prepare a project final report for Ecology review after all data collection activities and analytical data has been received. This report will summarize the methods used, procedures performed, analytical laboratory data, and lessons learned from the study. In addition, the report will include an interpretative section that details recommendations for stormwater BMPs. This report will be reviewed by Ecology staff and returned to EA for changes, with a final version due in two weeks. In addition, interim project reports describing progress to date can be prepared and submitted at Ecology's discretion.

Data Verification and Usability Assessment

The data verification assessment is the process of evaluating the completeness, correctness, and conformance/compliance of a given data set against the method, procedural, or contractual requirements (EPA 2002). This section describes the procedures used to verify the usability of obtained data for meeting project objectives.

Data verification

Analytical chemistry data will be examined for completeness, errors, and compliance with MPCs within one to two weeks of receiving the data. Laboratory compliance with QAPP requirements for sample condition upon receipt will be determined, as well as a comparison of QC results to standardized acceptance criteria and requirements. EA's QA coordinator will review laboratory and field logbooks and verify that all data planned for collection was obtained and that data entries are consistent and complete. Any deviations from established sampling designs, collection procedures, sample handling, and analytical methods will be evaluated for potential effects on the data validity. The follow measures will be evaluated during data verification:

- Sample holding times and receipt condition (i.e., temperatures of samples upon receipt)
- Sample detection and reporting limits
- Blank contamination (laboratory and field blanks)
- Accuracy (evaluation of matrix spike and check standard recoveries)
- Precision (evaluation of field and laboratory duplicate results)

The following guidelines will be applied when evaluated data does not meet established MPCs:

- Samples exceeding the holding time by > 48 hours will be rejected. Data from samples with holding time exceedances less than 48 hours will be qualified.

- Field and laboratory blank concentrations exceeding the reporting limits will be qualified and considered when evaluating samples from the corresponding batch.
- Duplicate results exceeding the project MPCs by more than twice the targeted value will be rejected.
- MS/MSD and LCS percent recovery values outside of the specific method limits represent uncertainty in the measured results and will be qualified.

Additionally, data that does not meet MPCs highlighted in the Quality Objectives section may be further qualified with the use of qualifiers as described below in Table 16.

Table 16. Data Qualifiers and Definitions

Data Qualifier	Definition
U	The analyte was not detected above the limit of detection
UJ	The analyte was not detected above the level of the limit of detection. The limit of detection value provided is an estimate and may be inaccurate or imprecise.
J	The analyte was detected. The provided value is an estimate of concentration of the analyte in the sample. J- or J+ indicate a low or high bias, respectively.
R	Sample results are rejected due to an inability to analyze sample or meet QC criteria. Presence or absence of the analyte cannot be confirmed.
NQ	Sample results are rejected due to an inability to analyze the sample. Presence or absence of the analyte cannot be confirmed.

Data usability assessment

Following data validation and verification, a data usability assessment is performed to determine whether data is suitable for meeting the project objectives. Data meeting the MPCs outlined in the Quality Objectives section will be considered usable provided the completeness of the data is adequate. For data that did not meet the defined MPCs, an assessment of data usability will be made which will consider representativeness and comparability. Uncertainty in the obtained data will be discussed in report deliverables.

Sampling design evaluation protocol

At present, there is limited available data for 6PPDQ in stormwater, soil, and following that would be useful in assessing variability in measured concentrations from this study and informing potential changes to the sampling design. Due to this limitation, power analysis was not conducted. This study is exploratory in nature; thus, the findings of the project will be used in developing future power analyses and sampling designs adequate to detect changes relating to stormwater treatment.

Data Analysis Methods

This section of the QAPP describes the data analysis methods anticipated to be used including handling of non-detect values, statistical approaches, and data presentation.

Handling of non-detect values

Where non-detect values represent a low proportion of the dataset (i.e., < 15%), non-detect values will be substitute with one half the detection limit. Where the proportion of non-detected values exceeds 15%, the R package NADA and maximum likelihood estimation (MLE) methods will be used to provide a more robust assessment of left-censored values (Helsel 2006; Shoari and Dubé 2018; US EPA 1998).

Data analysis methods

For both Task 4 and 5, the chemical removal efficiency for bioretention treatments will be calculated as follows:

Percent chemical removal = 1 – (Effluent concentration – influent concentration)/ (Influent concentration) *100

This metric will be calculated both for individual stormwater contaminants (i.e., 6PPDQ, copper, zinc, benzo(a)pyrene) and as totals for metals and PAHs.

For Task 4, the effect of soil type on concentrations of stormwater contaminants both among and within soils over time will be determined using repeated measures analysis of variance (ANOVA). This method accounts for the correlation within and between experimental treatments along with the time of the measurements (Muhammad 2023). In addition, Spearman's rank order correlation coefficient will be used to identify relationships between measured soil parameters and the degree of chemical removal provided by each soil treatment.

Similarly, data obtained from Task 5 will be analyzed using repeated measures ANOVA to determine the differences in chemical removal between and within soil-vegetation columns over time. The effect of stormwater exposure on vegetation growth (measured as plant height and lateral area) over time will be determined using repeated measures ANOVA. Non-parametric methods may be included if the datasets violate assumptions including an approximately normal distribution of the dependent variable and sphericity. The relationship between 6PPDQ and other stormwater contaminants (metals and PAHs) in all collected stormwater samples will be analyzed using linear regression.

All statistical tests and visualized will be conducted using R studio with α set at 0.05.

Data presentation

The data will be presented in a series of tables, charts, and graphs identifying the key results. For example, concentrations of 6PPDQ and other stormwater contaminants measured in the various soil types over time for Task 4 will be plotted using scatter and line plots to visualize changes over time. Overall, data presentation included in all reports will identify major trends, key findings, and any limitations of the project.

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Appendix A: Forms to Be Used

EA Engineering

CHAIN OF CUSTODY RECORD

No:

Lab:

Contact Phone:

Project Code:

Lab Contact:

Date Shipped:

Cooler #:

Lab Phone:

Lab #	Sample #	Location	Analyses	Matrix	Sample Date	Sample Time	Numb Cont	Container	Preservative	Lab QC

Special Instructions:	**SAMPLES TRANSFERRED FROM**
	CHAIN OF CUSTODY #

Items/Reason	Relinquished by (Signature and Organization)	Date/Time	Received by (Signature and Organization)	Date/Time	Sample Condition Upon Receipt

Chain of Custody Record & Laboratory Services Agreement

Alliance TECHNICAL GROUP
3600 Fremont Ave N. Seattle, WA 98103
Tel: 206-352-3790

Date: Page: of:

Laboratory Project No (internal):

Project Name:

Special Remarks:

Client:

Project No:

Address:

Collected by:

City, State, Zip:

Location:

Telephone:

Report To (PM):

Disposal: Samples will be disposed in 30 days unless otherwise requested.
☐ Retain volume (specify above) ☐ Return to client

Email(s):

Sample Name	Sample Date	Sample Time	Sample Type (Matrix)*	# of Cont.																	Comments
1																					
2																					
3																					
4																					
5																					
6																					

*Matrix: A = Air, AQ = Aqueous, B = Bulk, O = Other, P = Product, S = Soil, SD = Sediment, SL = Solid, W = Water, DW = Drinking Water, GW = Ground Water, SW = Storm Water, WW = Waste Water

**Metals (Circle): MTCA-5 RCRA-8 Priority Pollutants TAL *Individual:* Ag Al As B Ba Be Ca Cd Co Cr Cu Fe Hg K Mg Mn Mo Na Ni Pb Sb Se Sr Sn Ti Tl V Zn

***Anions (Circle): Nitrate Nitrite Chloride Sulfate Bromide O-Phosphate Fluoride Nitrate+Nitrite

Turn-around Time:
☐ Standard ☐ Next Day
☐ 3 Day ☐ Same Day
☐ 2 Day (specify)

I represent that I am authorized to enter into this Agreement with Alliance Technical Group LLC on behalf of the Client named above, that I have verified Client's agreement to each of the terms on the front and backside of this Agreement.

Relinquished (Signature)	Print Name	Date/Time	Received (Signature)	Print Name	Date/Time
x			x		
Relinquished (Signature)	Print Name	Date/Time	Received (Signature)	Print Name	Date/Time
x			x		

STORMWATER COLLECTION FIELD SHEET

PROJECT: _____ **PROJECT NO. :** _____

CLIENT: _____

FIELD PERSONNEL: _____

LOCATION: _____

FLOW CONDITIONS: _____

DATE: _____ **TIME:** _____

WEATHER: _____

Sample ID	Time of Collection	QA Sample	Container

NOTES: _____
_____
_____
_____
_____

Appendix B: SOPs

DEPARTMENT OF ECOLOGY
State of Washington

Collecting Grab Samples from Stormwater Discharges

Standard Operating Procedure
Version 1.2

March 2024

Publication 18-10-023

Publication and Contact Information

This document is available on the Department of Ecology's website at:
https://apps.ecology.wa.gov/publications/SummaryPages/1810023.html

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

Table of Contents

Washington State Department of Ecology

Standard Operating Procedure for Collecting Grab Samples from Stormwater Discharges

Version 1.2

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WQP001

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

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

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

SOP Revision History

Revision Date	Rev number	Summary of changes	Sections	Reviser(s)
6/29/2018	1.1	General updates to dates, references and website throughout. Safety section update.	All	Brandi Lubliner
1/11/2024	1.2	Recertification. Only version number and date changes	All	Brandi Lubliner

1.0 Purpose and Scope

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

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

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

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

2.0 Applicability

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

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

3.0 Definitions

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

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

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

3.4 **Intermediate Sampling Equipment**: Equipment other than the parameter-specific analytical sample bottle used to collect sample water. This equipment is typically used to collect sample water prior to pouring into the appropriate laboratory container and submitting the sample to the laboratory for analysis. Intermediate equipment can include Teflon or plastic water dippers, glass or plastic containers, Van Dorn samplers or Kemmerer Samplers. Note that equipment material must be compatible with the parameters sampled. Certain plastics should not be used when collecting some organic parameters, in

particular, oil and grease. Consult your laboratory or refer to bottle type material listed for each parameter in 40 Code of Federal Regulations (CFR) part 136.

4.0 Personnel Qualifications/Responsibilities

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

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

5.0 Equipment, Reagents, and Supplies

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

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

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

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

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

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

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

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

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

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

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

6.0 Summary of Procedure

6.1 Select a Representative Sampling Location

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

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

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

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

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

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

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

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

6.2 Pre-sampling Site Visit

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

6.2.1.1 Presence of debris

6.2.1.2 Signs of staining

6.2.1.3 Odors

6.2.1.4 Water/discharge discoloration

6.2.1.5 Unusual flows

6.2.1.6 Excessive sediment/solids deposits

6.2.1.7 Unexpected inflow pipes of unknown origin

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

6.2.3 Inspect the runoff stream for adequate depth for sampling.

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

6.2.4.1 Contributing land use drainage area

6.2.4.2 Presence/absence of illicit discharges and/or connections

6.2.4.3 All possible site hazards

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

6.3 Procedure Preparation

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

6.3.2 Gather appropriate equipment (see Equipment List).

6.4 Site Set-up Safety Procedures

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

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

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

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

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

6.5 Collecting Grab Samples from BMPs

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

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

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

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

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

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

6.6.2 Access sampling location

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

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

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

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

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

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

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

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

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

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

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

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

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

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

6.6.5.5 Follow steps 6.6.4.4 – 6.6.4.7 above.

6.7 Grab Sample Collection Procedures Using Intermediate Equipment

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

6.7.2 Access the sampling site.

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

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

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

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

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

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

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

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

6.7.11 Follow steps 6.6.4.4 – 6.6.4.7.

6.8 Labeling Sample Bottles

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

6.8.2 Station number

6.8.3 Date and Time

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

6.8.5 Preservatives added, if appropriate

6.8.6 Sampler's initials

6.9 Sample Processing

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

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

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

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

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

6.10 Sample Transport and Reporting/ Login Procedures

6.10.1 Complete Chain of Custody procedures.

6.10.2 For immediate delivery to the laboratory after sampling:

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

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

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

6.10.3 For samples shipped via air or ground freight service:

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

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

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

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

6.11 Decontamination

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

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

7.0 Records Management

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

7.1.1 Monitoring station location

7.1.2 Personnel - Initials of Sampling Personnel

7.1.3 Time of sample collection

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

7.1.5 Field observations that could affect the quality of the samples

8.0 Quality Control and Quality Assurance Section

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

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

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

9.0 Safety

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

9.2 Safety is top priority for field staff and supervisors. Sample sites may be located on or near roads and bridges. Roadside hazards, weather conditions, accidents, and construction should be evaluated before departure (especially in winter). If the hazard is a permanent condition,

relocation of the station may be necessary. Review periodically to assist with these safety determinations.

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

10.0 References

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

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

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

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

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

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

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

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

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

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

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

Appendix C. Glossaries, Acronyms, and Abbreviations

Glossary of General Terms

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

Anthropogenic: Human-caused.

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.

Reach: A specific portion or segment of a stream.

Riparian: Relating to the banks along a natural course of water.

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

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

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

Total 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.

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

Acronyms and Abbreviations

6PPDQ	N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine-quinone
ASTM	ASTM International
bgs	Below ground surface
BMP	Best management practice
BSM	Bioretention soil mix
CEC	Cation Exchange Capacity
EA	EA Engineering, Science, and Technology, Inc., PBC
EPA	U.S. Environmental Protection Agency
EB	Equipment blank
FB	Field blank
GC/MS	Gas Chromatography/Mass Spectrometry
HDPE	High-density polyethylene
K_{sat}	Saturated hydraulic conductivity
LB	Laboratory blank
LCS	Laboratory Control Sample
LID	Low Impact Development
MDL	Method Detection Limit
MS	Matrix spike
MSD	Matrix spike duplicate
PAH	Polycyclic aromatic hydrocarbon
PVC	Polyvinyl chloride
QA	Quality assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RPD	Relative Percent Difference

RL	Reporting Limit
SMMWW	Stormwater Management Manual for Western Washington
SPE	Solid Phase Extraction
SSC	Site Suitability Criteria
TWP	Tire wear particles

Units of Measurement

°C	degrees centigrade
cm	centimeter, a unit of length
cm/sec	centimeters per second, a unit of speed
dS/cm	decisiemens per centimeter, a unit of conductivity
G	gram, a unit of mass
g/cm^3	grams per cubic meter, a unit of density
in.	inches, a unit of length
in/hr	inches per hour
Kg	kilograms, a unit of mass equal to 1,000 grams
L	liters, a unit of capacity
m^3	cubic meters
mm	millimeters, a unit of length
meq/100g	milliequivalents per hundred grams of soil, a unit of cation exchange capacity
mg/kg	milligrams per kilogram (parts per million)
mg/L	milligrams per liter (parts per million)
mL	milliliter
ng/g	nanograms per gram (parts per billion)
ng/L	nanograms per liter (parts per trillion)

Quality Assurance Glossary

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

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

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

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

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

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

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

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

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

Continuing Calibration Verification Standard (CCV): A 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).

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

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

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

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

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

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

Examples of data types commonly validated would be:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Split sample: 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).

References for QA Glossary

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