Quality Assurance Project Plan for Stormwater Characterization for BMPs Study

March 2023

King County

Department of Natural Resources and Parks
Water and Land Resources Division
King County Environmental Lab
322 West Ewing Street
Seattle, WA 98119
206-477-7200 TTY Relay: 711
https://kingcounty.gov/depts/dnrp/wlr.aspx

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Prepared for:

King County Department of Natural Resources and Parks
Washington Department of Ecology

Submitted by:

Meghan Elkey
King County Environmental Laboratory
King County Water and Land Resources Division
Department of Natural Resources and Parks

Brandi Lubliner, P.E.
Washington State Department of Ecology
Water Quality Program

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King County
Department of
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Water and Land Resources Division

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Draft Quality Assurance Project Plan

Stormwater Characterization for BMPs Study

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Approved by:

Signature:	Date: 3/28/2023
Meghan Elkey, Laboratory Project Manager, King County Environmental Laboratory (KCEL)	
Signature: Keith Solberg (Mar 28, 2023 11:16 PDT)	Date: 3/28/2023
Keith Solberg, QA Officer, King County Environmental Laboratory	
Signature: Christopher Barnes (Mar 28, 2023 12:42 PDT)	Date: 3/28/2023
Christopher Barnes, Field Lead –KCEL, Field Sciences Unit	
Signature:	Date: 3/29/2023
Madison Rose Bristol, Project Manager, Washington Department of Ecology	
Signature:	Date: 3/31/2023
Brandi Lubliner, Quality Assurance Coordinator, Ecology	

1.0 BACKGROUND

This quality assurance project plan (QAPP) describes a pilot study to characterize stormwater runoff across storm events from a mixed highway and residential drainage area for concentrations of multiple contaminants, including the emerging contaminant 6PPD-quinone (6PPD-Q). Understanding the range of stormwater runoff concentrations of 6PPD-Q, a chemical that has been found to be acutely lethal to coho salmon (*Oncorhynchus kisutch*) and causes urban runoff mortality syndrome (URMS), is an important first step in designing treatment options for stormwater management. The project is funded by the Washington State Department of Ecology (Ecology). Both King County's technical objectives and Ecology's related project requirements are reflected in this QAPP.

1.1 Previous Study Information

Between 2007 and 2013, six National Pollutant Discharge Elimination System (NPDES) Phase I Municipal Separate Storm Sewer System (MS4) permittees and two ports were required under the permit Special Condition S8.D to extensively sample stormwater runoff flows and many pollutants over several years. These jurisdictions and Ecology established field sampling protocols for stormwater characterization from different land uses to standardize methodologies. This would ensure that the results were high quality, representative of storm event runoff in MS4s, and comparable across their jurisdictions, the Puget Sound region, and future studies. Their data reports provided highly representative storm event data representing stormwater quality across different land uses, storms, and seasons. Ecology compiled and analyzed all 8 datasets to provide a Western Washington regional baseline characterization of stormwater quality (Hobbs et al. 2015). These same protocols are still in use by MS4 permittees and Ecology funded stormwater studies to maintain consistency and comparability of data over time. A key finding was that even with consistent sampling and analysis protocols, the concentrations of pollutants in stormwater and in the entrained sediments vary widely – so much so across storms, jurisdictions, similar land uses, and seasons the authors concluded: *"…defining a 'typical' sediment or water contaminant composition for a particular land use is unrealistic. However, this analysis was successful in showing that statistically significant differences exist among land uses over multiple sample sites and parameters.*" While there may not be a 'typical' stormwater signal for any given storm, there are patterns of pollutants from different land uses that emerged and therefore can be used to design and implement stormwater management solutions.

Ecology administers the Technology Assessment Protocol-Ecology (TAPE) program, which is a peer-reviewed regulatory certification process for stormwater treatment technologies in operation since the late 1990s (Ecology, 2018a,b). Stormwater treatment technologies must be evaluated according to the prescribed sampling and evaluation protocols. Studies are done under an approved Quality Assurance Project Plan (QAPP) and the data is provided to the board of reviewers in the Technical Evaluation Report (TER) format. Ecology makes the final decision to certify new stormwater treatment technologies. Performance must be demonstrated by the technology proponent by testing their stormwater treatment technology under rainfall conditions typical of the Pacific Northwest and using TAPE protocols which are designed to evaluate flow through best management practices (BMPs). A TAPE certification means the BMP is approved for use on a development site to manage stormwater.

One critical element of doing BMPs treatment effectiveness studies is to know in advance the character of the contaminant concentration profile across the storm hydrograph, and in particular if enough of the contaminant is present in the stormwater discharge to be successfully treated. The stormwater runoff is the "influent" to the BMP being tested. Low contaminant concentrations in the influent are known to preclude a significant treatment finding result, and therefore knowledge of and some consistency in contaminants carried in stormwater runoff at BMP testing sites is necessary. Finding sites to reliably produce contaminant concentrations within the range needed for BMP testing has proven difficult for BMP proponents over time. Ecology and the Washington State Department of Transportation (WSDOT) have built a couple unique sites to facilitate stormwater BMP sampling. These dedicated testing facilities are at location where the stormwater can be easily and safely accessed and has enough contaminants for BMPs to reduce and meet statistical treatment objectives.

Recently, researchers have identified a new chemical in stormwater that forms from an antioxidant used in tires to extend their lifespan, that upon oxidation becomes 2-anilino-5-(4-methylpentan-2-ylamino)cyclohexa-2,5-diene-1,4-dione, a.k.a. 6PPD-quinone (6PPD-Q). This chemical is toxic to coho and is also toxic to several other aquatic species (Tian et al. 2021, 2022; Brinkmann et al. 2022; Hiki et al. 2021). To date, published studies that measure both 6PPD-Q concentration and toxicity to coho in field-collected stormwater are rare. Among the findings of Tian et al. (2021) was that the toxicity of 6PPD-Q to coho (as the LC_{50} value) differed by a factor of 3 in tire leachate samples diluted with two separate stormwater samples. In contrast, toxicity results for 6PPD-Q in two leachate solutions diluted with laboratory water were very consistent (Tian et al. 2021). Moreover, the toxicity of 6PPD-Q in stormwater in that experiment was both higher and lower than in the controlled leachate solutions. This result suggests that characteristics of the stormwater itself that were not measured in Tian et al.'s (2021) experiments affected toxicity of the 6PPD-Q. Stormwaters are complex mixtures of many chemicals (Ecology 2015), and although the reasons for differences in toxicity between Tian et al.'s (2021) two stormwater-diluted 6PPD-Q mixtures are unknown, variation in basic water quality parameters that are readily measured may provide useful insights.

2.0 PROJECT DESCRIPTION

2.1 Scope and Project Purpose

Little is known about 6PPD-Q concentrations in stormwater draining from different land uses in Washington State. This stormwater characterization pilot project will characterize the range of 6PPD-Q concentrations in stormwater runoff used for BMP testing at an established TAPE testing facility: the Ship Canal Testing Facility (SCTF). Stormwater will be collected as 2-3 stormwater grab samples across the storm hydrograph for up to 15 storms during Spring 2023 from the existing SCTF infrastructure (see Section 6 for more on field procedures).

This QAPP outlines the steps the Project Team intends to take to answer the research questions described below and provide data to Ecology. It includes data quality objectives (DQOs), method quality objectives (MQOs), study design, experimental procedures, and plans for quality control and data management. This pilot project will analyze these individual grab samples for a suite of parameters (see Section 5.3), including 6PPD-Q. Quality assurance of this contaminant data will be evaluated prior to June 30, 2023 to gain insights on the behavior and concentration profile of 6PPD-Q. From this work, Ecology expects to gain a better understanding of 6PPD-Q levels in runoff, which is an important first step to assess if existing field protocols for treatment evaluations of stormwater will need to be modified.

3.0 ORGANIZATION AND SCHEDULE

Table 1 summarizes staff involved in this project and responsibilities of each person.

Table 1. Organization of Project Staff and Responsibilities.

Title	Name	Affiliation	Responsibilities
Ecology Project Manager	**Madison Rose Bristol** Water Quality Program, Ecology **Phone**: (564) 669-4582	Washington Dept. of Ecology	Clarifies scope of the project. Provides internal review of QAPP and approves final QAPP.
Ecology Quality Assurance Officer	**Brandi Lubliner** Water Quality Program, Ecology **Phone**: (360) 407-7671	Washington Dept. of Ecology	Wrote introduction and reviews/approves draft QAPP and final QAPP.
KCEL Laboratory Project Manager	**Meghan Elkey** King County, Dept. of Natural Resources & Parks, Water & Land Resources Division **Phone:** (206) 477-7154	King County Environmental Laboratory	Manages and oversees laboratory analyses, coordinates with lab units. Responsible for preparing chemistry laboratory report.
King County Field Lead	**Christopher Barnes** King County, Dept. of Natural Resources & Parks, Water & Land Resources Division **Phone**: (206) 477-7143	King County Environmental Laboratory, Field Sciences Unit	Tracks weather and identifies storms for sampling, informs team as weather certainty improves, performs and oversees sample collection.

Target schedule milestones come from the interagency agreement with Ecology; C2300107 and are summarized in Table 2.

Table 2. Project Milestones.

Task	Target Date
Ecology-approved QAPP complete and final	February 28, 2023, or when QAPP approved
All laboratories prepared	
Assembly of laboratory and field reports	Ongoing through June 2023.
Submittal of Project Report	June 2023, unless extended by Ecology
Data interpretation and report assembly	June 2023, unless extended by Ecology
Final Interpretive Report complete	June 2023, unless extended by Ecology

4.0 QUALITY OBJECTIVES

This experiment does not have specified regulatory or other standards that determine analytical requirements. Quality objectives for this project are defined by those of the laboratories involved and requirements of their internal method protocols.

4.1 Measurement Quality Objectives

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

4.1.1 MQOs for Precision, Bias, Sensitivity

MQOs for precision, bias and sensitivity are the method performance metrics and criteria for acceptance that provide the basis for evaluating data quality and usability are described in Tables 7, 8, 9, 10, and 11. Collection of data on the water quality characteristics will be conducted using portable single- or multiparameter probes. MQOs for water quality characteristics are summarized in Table 3.

4.1.1.1 Precision

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

Laboratory analytical measurements: Targets for acceptable precision in terms of relative percent difference (RPD) or relative standard deviation (RSD), in Tables 8, 9, 10, and 11.

Real-time measurements: Measurement of the water quality characteristics will take place in the field and in the laboratory, using standard single- or multi-parameter probes. The precision of each probe and measurement type is described in Table 3.

Table 3. Measurement Quality Specifications for Water Quality Characteristics.

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

4.1.1.2 Bias

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

Laboratory analytical bias will be assessed the analysis of blanks, including method blanks, and instrument blanks (Tables 8, 9, 10, 11).

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

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

4.1.1.3 Sensitivity

Sensitivity is measured through reporting limit performance (for example, in a regulatory setting, the method detection limit (MDL) is often used to describe sensitivity). MDLs and reporting detection limits will be provided with each analytical data report. Sensitivity of water quality measurements is determined by the resolution of the instruments used (Tables 8, 9, 10, 11).

4.1.2 MQOs for Representativeness, Comparability, and Completeness

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

4.1.2.1 Representativeness

The sampling to be conducted for this project will generate stormwater from one location representing stormwater discharge of roadway runoff from an interstate highway. The resulting chemical dataset for untreated stormwater is expected to be representative of this specific river-roadway-storm event combination to be sampled. Results will not provide the basis for evaluating temporal variability of 6PPD-Q within a sampling location, other than across the storms systems sampled in 2023.

4.1.2.2 Comparability

Analytical results may be used in comparisons to 1) each other, among samples collected for this study, 2) results of similar surveys reported in the past or future by other local agencies or in the peer reviewed literature, 3) results of future surveys by King County, and 4) results of studies that document thresholds of potential toxicity to fish and other aquatic life. The primary means to ensure the project meets these comparability requirements is through the use of SOPs and standard methods. Methods to be employed during project are listed in Table 7. Copies of SOPs will be provided on request.

Additional steps that ensure comparability for the purposes listed above:

- Established sample handling protocols. Field personnel will consistently follow required sample handling protocols for the target analytes (Table 6).
- Assembled an experienced Project Team to plan and execute the program in a manner that minimizes interference from exogenous contamination, prevents and tracks potential chemical degradation during handling, and various other errors that can occur during execution of water sampling projects.

4.1.2.3 Completeness

For this study to be successful, stormwater runoff at the designated sampling location (Figure 1) from discrete storms will be collected. Samples will be collected for up to 15 storms before May 30, 2023. Achieving the Project Objectives (Table 2) will assure completeness.

4.2 Acceptance Criteria, Quality of Existing Data

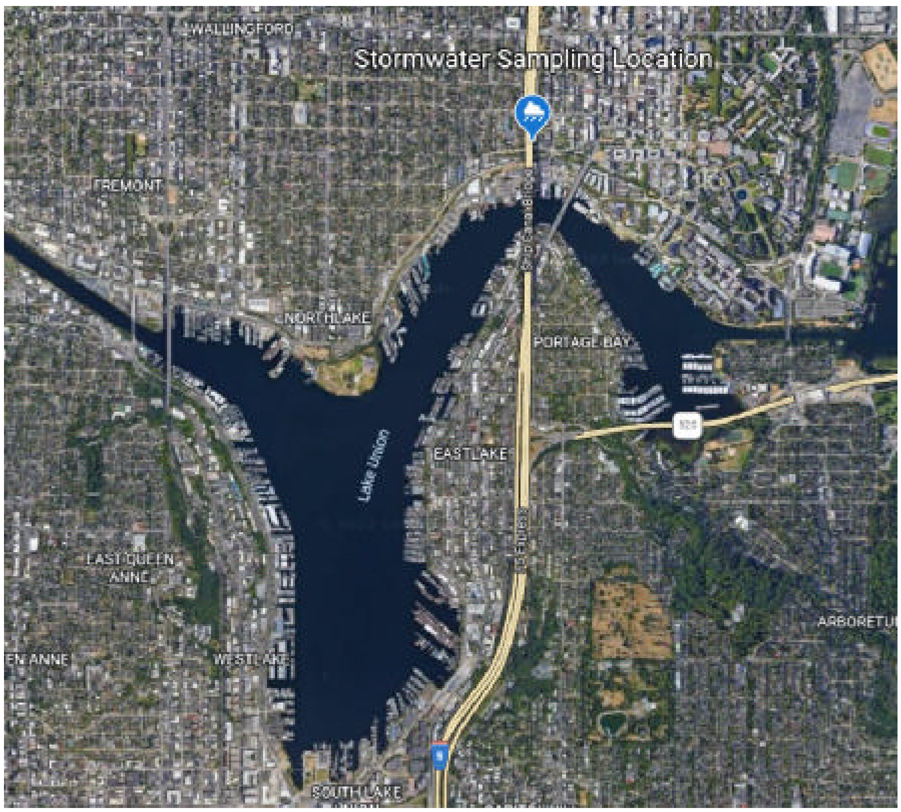
Most of the other parameters have been collected at this study location by other Ecology funded projects and will be referenced by Ecology to ascertain they fall within a typical range. This study is providing new and only pilot information on 6PPD-Q in runoff used at this site and therefore, we have not established acceptance criteria for the existing data to be used in interpreting and reporting results for this study.

5.0 SAMPLING DESIGN

5.1 Site Descriptions

The Ship Canal Testing Facility (SCTF) provides access to stormwater that drains directly from Interstate Highway 5 (I-5) and adjacent densely developed urban residential land. At this location, sampling can be safely performed using existing sampling infrastructure, including two vaults that receive a mix of right of way and paved runoff from I-5 above.

Figure 1. Stormwater sample collection location.



The stormwater samples will be collected from a single location (Figure 1) and consisting of runoff directly from I-5 during up to fifteen separate storms. GPS coordinates are: 47°39'22.6"N 122°19'19.8"W. Stormwater collection will be performed using available facilities at that location.

Figure 2. Stormwater sample collection visual.

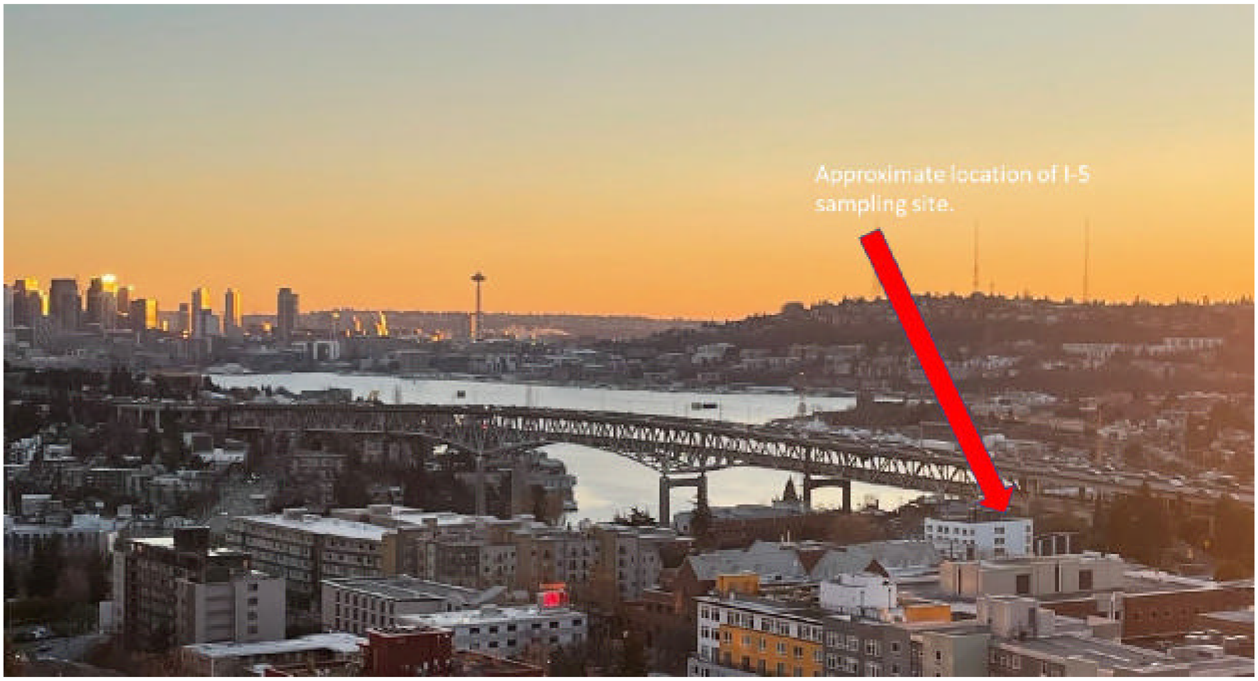


Figure 3. Stormwater sampling valve.

5.2 Qualifying Storm Event Criteria for Stormwater Sampling

Up to 15 qualifying storm events will be collected before May 30, 2023. Storm criteria for the wet season (October 1 through April 30) are: rainfall volume is at least 0.2 inches with no maximum, no maximum or minimum duration, antecedent dry period is less than or equal to .05 inch of rain in the previous 6 hours, and the inter-event dry period is 6 hours. Storm criteria for the dry season (May 1 through September 30) are: rainfall volume is at least 0.2 inches with no maximum, no maximum or minimum duration, antecedent dry period is less than or equal to 0.02 inch of rain in the previous 24 hours, and the inter-event dry period is 6 hours. Storm event criteria are summarized in Table 4.

Table 4. Storm criteria for stormwater sampling.

	Wet Season	Dry Season
Seasonal Period	October 1 through April 30	May 1 through September 30
Minimum Amount of Rainfall	0.20 min. no fixed max.	0.20 min. no fixed max.
Rainfall Duration	No fixed min. or max.	No fixed min. or max.
Antecedent Dry Period	< or equal to 0.05” rain in previous 6-hours	< or equal to 0.02” rain in previous 24-hours
Inter-event Dry Period	6 hours	6 hours

5.3 Parameters for Stormwater Sampling

Field measurements will be used for the following parameters:

- pH
- Conductivity
- Temperature

Grab samples will be analyzed for the following parameters:

- 6PPD-quinone
- Total Suspended Solids
- Orthophosphate Phosphorus
- Total Phosphorus
- Total Kjeldahl Nitrogen
- Total Nitrogen
- Nitrate-Nitrite Nitrogen
- Ammonia Nitrogen

- Total Organic Carbon
- Dissolved Organic Carbon
- Turbidity
- Hardness as $CaCO_3$
- Total Cadmium
- Dissolved Cadmium
- Total Copper
- Dissolved Copper
- Total Lead
- Dissolved Lead
- Total Zinc
- Dissolved Zinc
- PAHs
- PCBs
- Phthalates
- Semi-Volatile Petroleum Products (NWTPH-Dx)

6.0 SAMPLING PROCEDURES

6.1 Stormwater Monitoring Sampling Deployment

6.1.1 Monitor Forecast

Sampling staff will monitor the weather forecast. When antecedent conditions have been or will be met and the forecast is for a qualifying storm, the sampling staff will deploy for the upcoming event, provided there is sufficient time to complete sample during regular business hours.

6.1.2 Field Staff Sample Deployment

Once the decision is made to deploy, field staff will complete the following:

- Gather all materials for deployment which may include, sample bottle kit, peristaltic pump, batteries, coolers, calibrated EXO sonde, and ice.
- Proceed to sampling site (Figure 1).
- Collect grab samples from existing infrastructure. Perform filed measurements. Filter dissolved samples.
- Transport samples to KCEL.

Field staff will wear powder-free nitrile gloves for safe handling to prevent cross contamination of samples. Either ice or refrigerated samplers will be used to keep sample temperature within Ecology's guidelines (WQ-R-95-80 or most up to date).

Sampling staff should continue to monitor the targeted storm event throughout the event. The goal is to collect 2-3 grab samples per event - one at the start of the event, one toward the end of the event, and one during the event. If the storm event extends outside of work hours, samples will not be collected during that time.

6.2 Sample Collection and Handling Procedures

At these sampling intervals, sampling staff will collect field measurements and grab samples.

Grab samples will be collected during qualifying storms for all parameters. Also, pH, conductivity, and temperature data will be collected in the field during qualifying storms. However, if the timing of a storm event requires the collection of grab samples in unsafe conditions, such as when it's dark, or outside the lab's normal working hours, then the grab samples can be collected during another qualifying storm event.

King County will target up to 15 sampling events before May 30, 2023.

Once samples are collected, field staff will download rainfall data, and ensure the samples are cooled. Precipitation data will be collected from a rain gauge located within the drainage area of the stormwater monitoring site (UW rooftop -> http://www-k12.atmos.washington.edu/k12/grayskies/nw_weather.html).

Sampling staff will review the following information to determine if the sample is representative of the runoff event and the rain event meets storm criteria:

- Rainfall hydrograph (to determine if rainfall amount met storm criteria, e.g., 0.2 inches)

Once the storm event is determined to meet criteria, samples should be placed on ice with proper chain of custody forms. Each sample container will be filled to the appropriate level. Once sample volume has been collected, both the dissolved metals sample and the orthophosphorus sample will be filtered. Dissolved metals samples will be drawn through a cleaned Nalgene 500 mL filtration apparatus with 0.45 micron filters using a peristaltic pump. Orthophosphorus will be filtered using a 0.45 micron syringe filter.

If the sample collection crew is unable to filter the appropriate sub-samples immediately, the sample will be stored on ice and transported back to the King County Environmental Laboratory (KCEL) for filtration. Appropriate hold-time violation flags will be added to the data.

During sample preparation, all field quality assurance (QA)/quality control (QC) samples (duplicates, hold times) that require analysis should be recorded in field notebooks, on chain-of-custody forms and placed on ice in the same cooler with stormwater samples for laboratory delivery.

6.3 Field Data and COC Forms

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

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

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

In addition to LIMS numbers, descriptive sample identifiers (client locators) will be assigned to each sample. The field sheet will also be used to record general weather and any deviations from the sampling plan, excessively warm ambient outdoor temperatures and unexpectedly high turbidity in the stormwater sample.

Chain-of-custody (COC) forms should be used to accompany samples being transported to the subconsultant. These forms are typically provided by the laboratory and can include the following information:

- Sample time and date
- Preservatives used
- Name of sampler
- Analytical test method requested
- Parameter to be analyzed
- Coordination with bottle labels

6.4 Decontamination Procedures

Once samples are collected, all re-usable equipment should be decontaminated with wash and rinse water. EPA approved detergents and de-ionized water (ASTM I or II) should be used to provide efficient decontamination of equipment. Equipment blanks may be analyzed to check for possible cross contamination between sampling events. The amount of equipment blanks collected is optional, based on data quality objectives established earlier in this document.

Proper personal protective equipment (new powder-free gloves) should be worn during sampling activities and during decontamination processes. (For more information on decontamination procedures see KCEL SOPs 06-05-002-001 and 07-04-001-002).

6.5 Collection of QA\QC Samples

Table 5 provides a list of blanks that will be collected in the field to meet QAPP objectives.

Table 5. Quality control sample summary.

Blank Type	Frequency of Collection	Collection Procedure
Dissolved Metals field filtration blank	Every event	Carry Reverse Osmosis (RO) water to field and filter through field equipment during sample collection.
ORTHOP field filtration blank	Every event	Carry RO water to field and filter through field equipment during sample collection.

6.6 Periodic Preventative Maintenance

Periodic preventative maintenance of equipment can occur between storm events to ensure equipment is operating properly. Signs of vandalism, rusting equipment, equipment failure or other maintenance issues will be documented in field notebooks or on field data forms. Any significant changes in site conditions that will affect sampling should be revised in the QAPP.

7.0 MEASUREMENT PROCEDURES

7.1 Sample Volume, Containers, and Hold Time

Table 6 includes stormwater sample volume, container type, holding time and preservative needed for each required parameter. Sample volume requirements can also vary from laboratory to laboratory. Additionally, some parameters can be combined into one sample volume, reducing the need to collect individual samples for each parameter.

Table 6. Stormwater sample volume, container type, holding time, and preservation requirements.

Parameter	Recommended Quantity	Container	Holding Time	Preservation
6PPD-quinone	250 mL	250 mL amber glass	4 weeks	4°C (wet ice) in dark. Minimize head space, do not freeze
Total suspended solids	1 L	1 L WM HDPE	7 days	< 6°C
Turbidity	> 150 mL	500 mL WM HDPE	48 hours	< 6°C
Total phosphorus	250 mL	250 mL WM HDPE (together with total nitrogen)	28 days	Freeze at –20°C within 2 days of collection
Orthophosphate Phosphorus	60 mL	60 mL WM HDPE (together with ammonia and nitrate-nitrite)	14 days @ -20°C	Field filter within 15 minutes of collection. Freeze at –20°C within 1 day of collection
Total Kjeldahl Nitrogen	250 mL	250 mL WM HDPE	28 days	H_2SO_4 to pH < 2 within 15 minutes of collection
Total nitrogen	250 mL	250 mL WM HDPE (together with total phosphorus)	28 days	Freeze at –20°C within 2 days of collection
Nitrate-nitrite Nitrogen	60 mL	60 mL WM HDPE (together with ammonia and orthophosphate)	14 days @ -20°C	Freeze at –20°C within 1 day of collection

Ammonia Nitrogen	60 mL	60 mL WM HDPE (together with orthophosphate and nitrate-nitrite))	4 days @ -20°C	Freeze at –20°C within 1 day of collection
Total Organic Carbon	125 mL	125 mL Amber Glass	28 days	HCl to pH < 2 within 24 hours of collection
Dissolved Organic Carbon	125 mL	125 mL Amber Glass	28 days	0.45 µm filter and HCl to pH < 2 within 24 hours of collection
Total metals – hardness as $CaCO_3$, lead, zinc, copper, cadmium	500 mL	500 mL acid washed WM HDPE	180 days	HNO3 to pH < 2 within 24 hours of collection
Dissolved metals – zinc, lead, copper, cadmium	500 mL	500 mL acid washed WM HDPE	15 minutes for filtration and then 180 days for analysis	Field filter with acid washed 0.45 µm filter apparatus within 15 minutes of collection. Preserve with HNO3 to pH < 2 within 24 hours of collection
PAHs - subcontracted	1 L	1 L ANM Glass	7 days	< 6°C
Phthalates - subcontracted	1 L	1 L ANM Glass	7 days	< 6°C
PCBs - subcontracted	1 L	1 L ANM Glass	7 days	< 6°C
Semi-Volatile Petroleum Products (NWTPH-Dx) - subcontracted	1 L	1 L ANM Glass	7 days	< 6°C

7.3 Analytical Methods and Reporting Limits

The analytical methods selected for this project must correspond with those provided in Appendix 9 of the example Phase I permit and in the addition guidance Alternative Laboratory Methods Approved by Ecology for Use under the Phase I Municipal Stormwater Permit. Alternative analytical methods not listed in the above references may be used with prior approval by Ecology. Table 7 lists the analytical methods, method detection limits, and reporting detection limits that will be used for stormwater monitoring chemical analysis.

Table 7. Analytical methods, method detection limits, and reporting detection limits for stormwater analysis.

Parameter	Method	Method Detection Limit	Reporting Detection Limit
Conductivity, field	KCEL SOP #245v1	0.5 mS/cm	10 mS/cm
pH, field	KCEL SOP #245v1	N/A	N/A
Temperature, field	KCEL SOP #245v1	N/A	N/A
6PPD-quinone	KCEL SOP #4077	0.01 ug/L	0.05 ug/L
Turbidity	SM 2130-B	0.2 NTU	0.5 NTU
Total Suspended Solids	SM 2540-D	0.5 mg/L	2 mg/L
Total Phosphorus	SM 4500-P-B,F	0.005 mg/L	0.02 mg/L
Orthophosphate Phosphorus	SM 4500-P,F	0.0005 mg/L	0.002 mg/L
Total Kjeldahl Nitrogen	EPA 351.2	0.1 mg/L	0.4 mg/L
Total Nitrogen	SM 4500-N-C	0.05 mg/L	0.2 mg/L
Nitrate-nitrite Nitrogen	SM 4500-NO3-F	0.01 mg/L	0.04 mg/L
Ammonia Nitrogen	Kerouel & Aminot 1997	0.002 mg/L	0.01 mg/L
Total Organic Carbon	SM 5310-B	0.5 mg/L	2 mg/L
Dissolved Organic Carbon	SM 5310-B	0.5 mg/L	2 mg/L
Hardness as $CaCO_3$	SM 2340B	0.331 mg/L	0.331 mg/L
Cadmium, Total	EPA 200.8	0.05 ug/L	0.25 ug/L
Cadmium, Dissolved	EPA 200.8	0.05 ug/L	0.25 ug/L
Copper, Total	EPA 200.8	0.2 ug/L	2 ug/L
Copper, Dissolved	EPA 200.8	0.2 ug/L	2 ug/L
Lead, Total	EPA 200.8	0.1 ug/L	0.5 ug/L
Lead, Dissolved	EPA 200.8	0.1 ug/L	0.5 ug/L

Zinc, Total	EPA 200.8	0.5 ug/L	2.5 ug/L
Zinc, Dissolved	EPA 200.8	0.5 ug/L	2.5 ug/L
PAHs and Phthalates - subcontracted			
Phenol	EPA 8270E	0.0100 ug/L	0.200 ug/L
bis(2-chloroethyl) ether	EPA 8270E	0.0280 ug/L	0.200 ug/L
2-Chlorophenol	EPA 8270E	0.0290 ug/L	0.200 ug/L
1,3-Dichlorobenzene	EPA 8270E	0.0310 ug/L	0.200 ug/L
1,4-Dichlorobenzene	EPA 8270E	0.0280 ug/L	0.200 ug/L
1,2-Dichlorobenzene	EPA 8270E	0.0330 ug/L	0.200 ug/L
Benzyl Alcohol	EPA 8270E	0.0230 ug/L	0.200 ug/L
2,2'-Oxybis(1-chloropropane)	EPA 8270E	0.0280 ug/L	0.200 ug/L
2-Methylphenol	EPA 8270E	0.0270 ug/L	0.200 ug/L
Hexachloroethane	EPA 8270E	0.0370 ug/L	0.200 ug/L
N-Nitroso-di-n-Propylamine	EPA 8270E	0.0350 ug/L	0.200 ug/L
4-Methylphenol	EPA 8270E	0.0290 ug/L	0.200 ug/L
Nitrobenzene	EPA 8270E	0.0270 ug/L	0.200 ug/L
Isophorone	EPA 8270E	0.0310 ug/L	0.200 ug/L
2-Nitrophenol	EPA 8270E	0.0360 ug/L	1.00 ug/L
2,4-Dimethyphenol	EPA 8270E	0.270 ug/L	1.00ug/L
Bis(2-Chloroethoxy)methane	EPA 8270E	0.0300 ug/L	0.200 ug/L
2,4-Dichlorophenol	EPA 8270E	0.100 ug/L	1.00 ug/L
1,2,4-Trichlorobenzene	EPA 8270E	0.0320 ug/L	1.00 ug/L
Naphthalene	EPA 8270E	0.0250 ug/L	0.200 ug/L

Benzoic acid	EPA 8270E	0.130 ug/L	2.00 ug/L
4-Chloroaniline	EPA 8270E	0.0420 ug/L	1.00 ug/L
Hexachlorobutadiene	EPA 8270E	0.0380 ug/L	0.200 ug/L
4-Chloro-3-Methylphenol	EPA 8270E	0.130 ug/L	1.00 ug/L
2-Methylnaphthalene	EPA 8270E	0.0290 ug/L	0.200 ug/L
Hexachlorocyclopentadiene	EPA 8270E	0.140 ug/L	1.00 ug/L
2,4,6-Trichlorophenol	EPA 8270E	0.160 ug/L	1.00 ug/L
2,4,5-Trichlorophenol	EPA 8270E	0.130 ug/L	1.00 ug/L
2-Chloronaphthalene	EPA 8270E	0.0300 ug/L	0.200 ug/L
2-Nitroaniline	EPA 8270E	0.170 ug/L	1.00 ug/L
Acenaphthylene	EPA 8270E	0.0200 ug/L	0.200 ug/L
Dimethylphthalate	EPA 8270E	0.0350 ug/L	0.200 ug/L
2,6-Dinitrotoluene	EPA 8270E	0.170 ug/L	1.00 ug/L
Acenaphthene	EPA 8270E	0.0290 ug/L	0.200 ug/L
3-Nitroaniline	EPA 8270E	0.150 ug/L	1.00 ug/L
2,4-Dinitrophenol	EPA 8270E	0.220 ug/L	2.00 ug/L
Dibenzofuran	EPA 8270E	0.0200 ug/L	0.200 ug/L
4-Nitrophenol	EPA 8270E	0.0560 ug/L	1.00 ug/L
2,4-Dinitrotoluene	EPA 8270E	0.110 ug/L	1.00 ug/L
Fluorene	EPA 8270E	0.0210 ug/L	0.200 ug/L
4-Chlorophenylphenyl ether	EPA 8270E	0.0200 ug/L	0.200 ug/L
Diethyl phthalate	EPA 8270E	0.0600 ug/L	0.200 ug/L
4-Nitroaniline	EPA 8270E	0.170 ug/L	1.00 ug/L

4,6-Dinitro-2-methylphenol	EPA 8270E	0.360 ug/L	2.00 ug/L
N-Nitrosodiphenylamine	EPA 8270E	0.0250 ug/L	0.200 ug/L
4-Bromophenyl phenyl ether	EPA 8270E	0.0190 ug/L	0.200 ug/L
Hexachlorobenzene	EPA 8270E	0.0360 ug/L	0.200 ug/L
Pentachlorophenol	EPA 8270E	0.140 ug/L	1.00 ug/L
Phenanthrene	EPA 8270E	0.0210 ug/L	0.200 ug/L
Anthracene	EPA 8270E	0.0280 ug/L	0.200 ug/L
Carbazole	EPA 8270E	0.0370 ug/L	0.200 ug/L
Di-n-Butylphthalate	EPA 8270E	0.0510 ug/L	0.200 ug/L
Fluoranthene	EPA 8270E	0.0330 ug/L	0.200 ug/L
Pyrene	EPA 8270E	0.0310 ug/L	0.200 ug/L
Butylbenzylphthalate	EPA 8270E	0.0660 ug/L	0.200 ug/L
Benzo(a)anthracene	EPA 8270E	0.0370 ug/L	0.200 ug/L
3,3’-Dichlorobenzidine	EPA 8270E	0.340 ug/L	1.00 ug/L
Chrysene	EPA 8270E	0.0350 ug/L	0.200 ug/L
bis(2-Ethylhexyl)phthalate	EPA 8270E	0.163 ug/L	0.200 ug/L
Di-n-Octylphthalate	EPA 8270E	0.0450 ug/L	0.200 ug/L
Benzofluoranthenes, Total	EPA 8270E	0.0800 ug/L	0.400 ug/L
Benzo(a)pyrene	EPA 8270E	0.0490 ug/L	0.200 ug/L
Indeno(1,2,3-cd)pyrene	EPA 8270E	0.0560 ug/L	0.200 ug/L
Dibenzo(a,h)anthracene	EPA 8270E	0.0650 ug/L	0.200 ug/L
Benzo(g,h,i)perylene	EPA 8270E	0.0410 ug/L	0.200 ug/L
1-Methylnaphthalene	EPA 8270E	0.0260 ug/L	0.200 ug/L

PCBs - subcontracted			
Aroclor 1016	EPA 8082A	0.0175 ug/L	0.100 ug/L
Aroclor 1221	EPA 8082A	0.0175 ug/L	0.100 ug/L
Aroclor 1232	EPA 8082A	0.0175 ug/L	0.100 ug/L
Aroclor 1242	EPA 8082A	0.0175 ug/L	0.100 ug/L
Aroclor 1248	EPA 8082A	0.0175 ug/L	0.100 ug/L
Aroclor 1254	EPA 8082A	0.0175 ug/L	0.100 ug/L
Aroclor 1260	EPA 8082A	0.0174 ug/L	0.100 ug/L
Aroclor 1262	EPA 8082A	0.0174 ug/L	0.100 ug/L
Aroclor 1268	EPA 8082A	0.0174 ug/L	0.100 ug/L
Semi-Volatile Petroleum Products - subcontracted			
Diesel Range Organics (C12-C24)	NWTPH-Dx	0.0330 mg/L	0.100 mg/L
Motor Oil Range Organics (C24-C38)	NWTPH-Dx	0.0560 mg/L	0.200 mg/L

8.0 QUALITY CONTROL

8.1 Field Measurements

The sonde used for field measurements will be calibrated prior to the event, and there will be a post event end check. These will be documented on the field QC sheet.

8.2 Aquatic Toxicology

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

Table 8. Aquatic toxicology QC samples.

Parameters	Method Blank	Lab Duplicate %RPD	Matrix Spike %Recovery	Spike Blank %Recovery
6PPD-quinone	<MDL	40%	50-150%	50-150%

8.3 Conventionals

Laboratory QC samples for conventional analyses and associated control limits are summarized below. These QC samples will be analyzed at a frequency of one per analytical batch of 20 or fewer samples.

Table 9. Conventionals QC samples.

Parameters	Method Blank	Lab Duplicate %RPD	Spike Blank %Recovery	Matrix Spike %Recovery	Lab Control Sample %Recovery
Total suspended solids	<MDL	25%	N/A	N/A	80-120%
Turbidity	N/A	25%	N/A	N/A	90-110%
Total Phosphorus	<MDL	20%	80-120%	75-125%	85-115%
Orthophosphate Phosphorus	<MDL	20%	80-120%	75-125%	85-115%
Total Kjeldahl Nitrogen	<MDL	20%	80-120%	70-130%	80-120%

Total Nitrogen	<MDL	20%	80-120%	75-125%	85-115%
Nitrate-nitrite Nitrogen	<MDL	20%	80-120%	75-125%	85-115%
Ammonia Nitrogen	<MDL	20%	80-120%	75-125%	85-115%
Total Organic Carbon	<MDL	20%	80-120%	75-125%	85-115%
Dissolved Organic Carbon	<MDL	20%	80-120%	75-125%	85-115%

8.4 Metals

Laboratory QC samples for trace metals analyses and associated control limits are summarized below. These QC samples will be analyzed at a frequency of one per analytical batch of 20 or fewer samples.

Table 10. Metals QC samples.

Parameters	Method Blank	Lab Duplicate %RPD	Matrix Spike %Recovery	Spike Blank %Recovery
Dissolved Metals	< MDL	20%	75-125%	85-115%
Total Metals and Hardness	< MDL	20%	75-125%	85-115%

8.5 Organics

Laboratory QC samples for trace metals analyses and associated control limits are summarized below. All organics parameters will be subcontracted to ARI Labs. These QC samples will be analyzed at a frequency of one per analytical batch of 20 or fewer samples.

Table 11. Organics QC samples.

Parameters	Method Blank	Lab Duplicate %RPD	Matrix Spike %Recovery	Spike Blank %Recovery
PAHs	<MDL	30%	30-160%	30-160%

Phthalates	<MDL	30%	30-160%	30-160%
PCBs				
PCBs – all	<MDL	30%	N/A	N/A
Aroclor 1016	<MDL	30%	51-120%	51-120%
Aroclor 1260	<MDL	30%	56-120%	56-120%
Semi-Volatile Petroleum Products (NWTPH-Dx)				
Diesel Range Organics (C12-C24)	<MDL	30%	56-120%	56-120%
Motor Oil Range Organics (C24-C38)	<MDL	30%	30-160%	30-160%

8.6 Laboratory Quality Assurance/Quality Control Samples

Laboratory analytical quality control (QC) procedures involve the use of four basic types of QC samples. QC samples are analyzed within a batch of client samples to provide an indication of the performance of the entire analytical system. Therefore, QC samples go through all sample preparation, clean up, measurement, and data reduction steps in the procedure. In some cases, the laboratory may perform additional tests that check only one part of the analytical system.

8.7 Types of Laboratory Quality Control Samples

8.7.1 Check Standards

Check standards are QC samples of known concentration prepared independently of the calibration standards. They are sometimes called laboratory control samples (LCS) or laboratory fortified blanks (LFBs). Results are used to verify that analytical precision is in control and whether the level of bias due to calibration is acceptable. If the results for the check standards do not fall within established control limits, the measurement system should be re-calibrated. In some analytical methods, sample results may be qualified when associated check standard results are not within acceptable limits. Check standards are usually prepared in de-ionized water by the laboratory. Their concentration should be in the range of interest for the samples, and at least one check standard should be analyzed with each batch of 20 samples or fewer. Reference materials that more closely match the matrix of environmental samples may be used as check standards for the project. Some proficiency testing (PT) samples from commercial vendors can be stored and used as check standards once the true values are known. The acceptance limits for the results of analyses of these commercial samples should not be those set by the vendor but should be established in the laboratory by replicate analyses of the PT sample. An exception may occur when reference materials are sent to the laboratory for analysis as blinds. Ecology’s Laboratory Accreditation Section can help identify suppliers of PT samples and certified reference materials.

8.7.2 Laboratory Duplicates

The laboratory can analyze duplicate samples of one or more samples within each sample batch. Results are used to estimate analytical precision for that matrix at that concentration. The project manager may specify which samples are to be analyzed in duplicate. If the samples selected for duplicate analyses do not contain measurable amounts of the analyte of interest, the results provide no information on precision.

8.7.3 Matrix Spikes

A matrix spike is an aliquot of a sample to which a known amount of analyte is added at the start of the procedure. Matrix spike recoveries may provide an indication of bias due to interference from components of the sample matrix. Since the percent recovery is calculated from the difference between the analytical results for the spiked and un-spiked samples, its precision may be relatively poor if the spiked amount is much less than the sample concentration. If the spike is too high relative to the sample concentration, any interference effect at the sample concentration level could be masked. The laboratory will spike at a concentration approximately equal to the concentration in the sample before spiking. The project manager may indicate to the laboratory, which samples might be most appropriate for use as matrix spikes and, if necessary, larger sample volumes will be provided to the laboratory for this purpose. In some cases, many replicate spikes would need to be analyzed in order to distinguish bias from the effects of random error on the recoveries. Matrix spike results will only be used in conjunction with other QC data to qualify them. The primary use of matrix spikes is to indicate the presence of bias, duplicate spike results can be used to estimate analytical precision at the concentration of the spiked samples. The project manager may instruct the laboratory to spike certain samples since matrix spikes are not automatically included in all analytical methods.

8.7.4 Method Blanks

Method blanks, typically Reverse Osmosis (RO) water, are prepared and analyzed in the laboratory to document the response of the measurement system to a sample containing effectively none of the analyte of interest. Depending on the analytical method, the analyst will analyze one or more blanks with each batch of samples and compare the results to established acceptance limits. A positive blank response can be due to a variety of factors related to the procedure, equipment, or reagents. Unusually high blank responses indicate laboratory contamination. The blank response becomes very important when the analyte concentration is near the detection limit. Blank responses are sometimes used to correct the sample responses and to determine the limit of detection.

8.8 Types of Field Quality Control Samples

8.8.1 Field Replicates

Replicates are two samples collected at the same time and place. Replicate results provide a way to estimate the total random variability (precision) of individual results. If conditions in the medium being measured are changing faster than the procedure can be repeated, then the precision calculated from replicate results will include that variability as well.

8.8.2 Field Blanks

Field blanks are samples of “clean” material, which are exposed to sample collection procedures in the field. They should be analyzed like any other sample. The results for field blanks may indicate the presence of contamination due to sample collection and handling procedures (in the field or during transport to the laboratory) or to conditions in the field, such as boat or vehicle exhaust. Clearly identify field blanks so that they are not selected for analytical duplicates or matrix spikes. Field blanks are used when there is reason to expect problems with contamination or to meet programmatic or contractual requirements to demonstrate absence of contamination. Field blanks can be used to determine whether consistent and adequate field procedures are conducted during sampling. The use of good operational procedures in the field and thorough training of field staff reduces the risk of contamination. Several types of field blanks are described below. The R.O. water or other "clean" material used to prepare them must be obtained from the laboratory or other reliable supplier.

Field blanks can include:

- Equipment blanks: Prepare by exposing clean material to the sampling equipment after the equipment has been used in the field and cleaned. The results provide a check on the effectiveness of the cleaning procedures. The rinsate blank may also detect contamination from the surroundings, from containers, or from cross-contamination during transportation and storage of the samples and is therefore the most comprehensive type of field blank.
- Filter blanks: Prepare by filtering R.O. water through the filtration apparatus after routine cleaning. The filter blank may detect contamination from the filter or other part of the filtration apparatus. Ideally, the results for your field blanks will be "not detected." If the results are positive, you will need to consider them when reporting sample results and determining whether your MQOs have been met.
- Field filtration blank: (e.g., field filtration blank for orthophosphorus or dissolved metals filtration) Carry R.O. water into the field and filter using field equipment.

9.0 DATA QUALITY, ASSESSMENT, QUALIFICATION, AND REPORTING

Data reported by the lab, including field measurements, must pass a review process before final results are available to the client. A "Peer Review" process is used where a second analyst or individual proficient at the method reviews the data set. The reviewer will complete a data review checklist which will document the completeness of the data package and if any QC failures exist. The Laboratory Project Manager will coordinate this data review.

Once data review is complete and all data quality issues have been resolved or corrected, the status of the data in LIMS will be changed to "approved". Once a data set has been approved, it is "posted" or transferred to the portion of the LIMS database known as the Environmental Data System (EDS) where all historical LIMS data are maintained. Signatures or initials of the lab lead and reviewer(s) indicate formal approval of hardcopy data or reports (non-LIMS), typically on the review checklist. A copy of this approved checklist should be stored with the final hardcopy data package.

King County will retain records of all monitoring information, including all calibration and maintenance records and all original recordings for continuous monitoring instrumentation, copies of all reports required by this permit, and records of all data used to complete the application for this permit, for a period of at least five years.

9.1 Data Storage

Data will not be distributed outside each lab unit or to clients until it has met the full definition of final data. "Final Data" is defined as approved data posted to the historical database (EDS) or is otherwise in its final reportable and stored format (if not a LIMS parameter). This implies the data has been appropriately peer reviewed, properly qualified and is in its final format in terms of units and significant figures. Not only is final data assured of a higher level of quality through peer reviewing and qualification, but it will also match any future reports since it has come from the final storage location.

9.2 Data Reduction, Review, and Reporting

All lab and field measurements will follow the procedures outlined in the KCEL's SOPs and QA Manual. Laboratory staff will be responsible for internal quality control verification, proper data transfer, and reporting data to the Project Manager via the Laboratory Information Management System (LIMS).

The results report will include:

- An analytical report for the chemistry analysis
- A quality control (QC) report
- Documentation of any invalid or anomalous test results
- Chain of custody forms
- Field sheets

9.3 Proposed Laboratory Qualifiers

Qualifiers will be applied to water quality data during the data quality review process.

Table 12. Laboratory qualifiers.

Qualifier	Description
General	
H	Indicates that an analysis holding time criterion was not met.
SH	Indicates that a sample handling criterion was not met. The sample may have been compromised during the sampling procedure or may not comply with storage conditions or preservation requirements.
R	Indicates that the data are judged unusable by the data reviewer. The qualifier is applied based on the professional judgment of the data reviewer rather than any specific set of QC parameters and is applied when the reviewer feels that the data may not or will not provide any useful information to the data user.
<MDL	Applied when a target analyte is not detected or detected at a concentration less than the associated method detection limit (MDL). The MDL is the lowest concentration at which a sample result will be reported.
<RDL	Applied when a target analyte is detected at a concentration greater than or equal to the associated MDL but less than the associated reporting detection limit (RDL). RDL is defined as the lowest concentration at which an analyte can reliably be quantified.
RDL	Applied when a target analyte is detected at a concentration that, in the raw data is equal to the RDL.
TA	Applied to a sample result when additional narrative information is available in the text field. The additional information may help to qualify the sample result but is not necessarily covered by any other qualifier.
Chemistry	
B or B3	Applied to a sample result when an analyte was detected at a concentration greater than the MDL in the associated method blank. The qualifier is applied when the sample concentration is >MDL but less than ten times the blank concentration. The qualifier indicates that the analyte concentration in the sample may be significantly influenced by laboratory contamination.
E	Applied to a sample result that was measured at a concentration greater than the calibration range of the method. It is applied when the detected analyte concentration exceeds the upper instrument calibration limit and further dilution is not feasible. The reported value is an estimated analyte concentration.
J	Applied to a sample result that is considered an estimated value.
JG	Applied to a sample result that is considered an estimated value with a low bias. This will typically be applied when QC results indicate the recovery of the analyte is below the expected limits of the method.
JL	Applied to a sample result that is considered an estimated value with a high bias. This will typically be applied when QC results indicate the recovery of the analyte is above the expected limits of the method.

10.0 REFERENCES

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Quality Assurance Project Plan for Stormwater Characterization for BMPs Study - KCEL Signatures

Final Audit Report 2023-03-28

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  Signature Date: 2023-03-28 - 6:16:32 PM GMT - Time Source: server

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