Quality Assurance Project Plan: Bioretention Capture Efficacy of PCBs from Stormwater– RSMP Effectiveness Study

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King County

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Quality Assurance Project Plan: Bioretention Capture Efficacy of PCBs from Stormwater–RSMP Effectiveness Study

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Submitted by:

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APPROVALS

Richard Jack, King County Project Manager	Date
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Colin Elliott, King County Environmental Laboratory Quality Assurance Officer	Date
Brandi Lubliner, Washington State Department of Ecology	Date
Bill Moore, Washington State Department of Ecology	Date

Certification

I certify under penalty of law, that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gathered and evaluated the information submitted. Based on my inquiry of the person or persons who manage the system or those persons directly responsible for gathering information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for willful violations.

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1.0 BACKGROUND

The Regional Stormwater Monitoring Program (RSMP) is a collaboration of western Washington municipal stormwater permittees, state, and federal agencies. The Stormwater Work Group (SWG) oversees the implementation of the RSMP. The RSMP was designed to meet MS4 permittee stormwater monitoring needs. Further, the RSMP provides a structure that allows permittees to pool resources and conduct effectiveness studies to improve municipal stormwater management. The goals of RSMP effectiveness studies are to measure the effectiveness of various stormwater management activities, best management practices (BMPs), and to communicate findings to the regions' professionals.

The 2013–2018 Western Washington Phase I and Phase II Municipal Stormwater General Permits (permits) require the use of Low Impact Development (LID) where feasible and bioretention is a commonly utilized LID BMP in Western Washington. Some jurisdictions also use the term "rain gardens," which are informally designed and built bioretention-like structures. Because rain gardens are not engineered structures under the stormwater permits, their variable properties are not the focus of this project. Bioretention facilities have design specifications which are described under BMP T7.30 in the Washington State Department of Ecology's (Ecology) Stormwater Management Manual for Western Washington (SMMWW). The default bioretention soil mixture (BSM) is 60% sand, 40% compost (Ecology, 2012). The focus of this study is to evaluate the degree to which the default BSM removes polychlorinated biphenyls (PCBs) from stormwater. The study goals are to determine if PCBs are captured from stormwater by the BSM, and to estimate the efficacy of capture and retention of PCBs over a two-year period. The degree to which PCB's are captured and retained by BSM in the Pacific Northwest is currently unknown.

Funding for this project comes from the municipal stormwater permittees via the RSMP. Results are also intended to inform regional stormwater managers, Ecology, and other researchers conducting studies on bioretention soil mixtures.

1.1 PCBs Background and Relevant Environmental Behavior

Production of PCBs was banned in the United States under the Toxic Substances Control Act in 1977 (15 USC 2605[e]); they are typically considered a legacy contaminant. However, despite this ban, PCBs remain in current use products (like caulks and paints [SAIC 2011]) and persist in a variety of environmental reservoirs such as contaminated soils, sediments, water bodies, and fish tissue due to their long half-lives (i.e., months to years) (Ayris and Harrad 1999). Individual chlorinated biphenyl molecules are called congeners and are identified by the number and position of the chlorine atoms around the biphenyl rings. There are 209 possible PCB congeners. When manufactured, PCBs were made by passing chlorine gas over a mixture of biphenyl molecules; this produced a mix of congeners and these mixtures were sold as products called Aroclors. Some individual PCB congeners are still incidentally produced during the manufacture of other chemicals

(Rodenburg et al. 2010). These congeners can be found at low levels in numerous products; yellow inks are particularly noteworthy for their incidental PCB content.

PCBs are semi-volatile, meaning they can volatilize from environmental reservoirs and consumer products. Atmospheric transport and redeposition of PCBs is a well-documented phenomenon, especially in colder northern climates where snow scavenging of atmospheric PCBs is especially prominent (Wania et al. 1998, Daly and Wania 2004). Atmospheric PCBs also readily sorb onto the "organic film" on urban surfaces (Diamond et al. 2000, Simpson et al. 2005). These physical and chemical attributes contribute to the prevalence of PCBs in urban stormwater and substantial urban stormwater loads (Parsons and Terragraphics 2007, King County 2013).

Over 180 water bodies in Washington State are classified as impaired due to elevated PCB concentrations in sediment, water, and fish tissue. In addition, the Washington Department of Health (WADOH) has established 14 fish consumption advisories based on elevated PCB levels in fish or shellfish. A recent study determined that urban stormwater contributes roughly 60% of the total PCB load to Lake Washington, while direct atmospheric deposition of PCBs contributes 14%; combined they represent about three-quarters of the total loading (King County 2013). Four quarterly samples in 2011–2012 documented total PCB concentrations in runoff from the I-90 floating bridge between 3,300 and 16,000 pg/L.

Literature on the PCB load reducing performance of bioretention BMPs is limited. One rain garden study in San Francisco documented the successful removal of 80+% of the PCBs from urban stormwaters (Gilbreath et al. 2012). Dissolved PCBs bind to their organic carbon fraction of BSM, usually provided by compost, while the highly permeable sand filters out particulate associated PCBs. However, a number of laboratory, field, and chemical modeling studies have demonstrated that PCBs can also readily volatilize from soils to the atmosphere (Harner et al. 1995, Kurt-Karakus and Jones 2006, Cabrerizo et al. 2011, Hippelein and McLachlan 1998, Hippelein and McLachlan 2000). No study to date has addressed the question of overall year-to-year effectiveness of BSM to capture and retain PCBs from stormwater. Soil loss studies and models further suggest that PCBs captured by bioretention soils will in part volatilize and cycle back to the urban environment.

To understand BSM capability to remove and retain PCBs, this project will document the retention of PCBs in BSM by measuring PCBs levels in bioretention soils over time and the stormwater flowing into and out of a bioretention study cell (also called a mesocosm). There will likely be loss of PCBs from the BSM due to volatilization; however, this project will not directly measure PCB losses. The goal of this study is to evaluate for the first time: a common stormwater BMP's efficacy to remove PCBs from Western Washington urban stormwater, and document the multiyear effectiveness of PCB sequestration in BSM.

There is significant regional interest in developing and understanding bioretention soil mixes that effectively treat common stormwater pollutants. This project shares a study design and facilities with another RSMP project looking at improving the default BSM with fungal soil amendments. The companion study is being conducted by Washington State

University and the US Fish and Wildlife Service (WSU/USFWS). Taylor et al. (2016) describes their project.

Because the chemical properties of PCBs vary by congener, evaluation of PCB losses from the mesocosms through volatilization or outflows will be based on both an individual congener basis, as well as total PCBs (sum of detected congeners). The congener specific mass balance will provide a conceptual model of PCB congener behavior in the mesocom bioretention cells with and without plants. Combined, the conceptual model and mass balance will describe the potential effectiveness of Western Washington bioretention cells to reduce PCB loadings to receiving water bodies. PCB degradation in soils is minimal due to the approximately seven-year half-life of PCBs in soils (Sinkkonen and Paasivirta 2000). Soil degradation rates in the conceptual model may be estimated using published literature.

Ensuring that bioretention BMPs address PCBs, a stormwater pollutant of high public health concern, is important to ensure that investments in retrofits reduce the circulation of PCBs in the environment. The project will inform Ecology and stormwater permittees regarding the efficacy of the bioretention BMP (T7.30) in the SMMWW (Ecology 2014) and the Rain Garden Design Manual (Hinman 2013). These guidance documents are heavily utilized by permit writers and municipal stormwater managers. This information will help Ecology and permittees use state-of-the-art technology and the best available science.

1.2 Mesocosm System Design

This study is using biorentention mesocosms built by WSU/USFWS (Taylor et al. 2016). Briefly, they are stainless steel 55-gallon drums with BSM, a gravel underdrain, and a 2-inch slotted PVC outlet. Approximately 18-inches of 60/40 BSM is above the underdrain layer. All sands, composts, and gravels used in their construction, along with their compaction and permeability, conform to SMMWWW BMP T7.30 specifications.

This study will use a multichannel pump to deliver the equivalent of a 6 month 24-hour storm event to each mesocosm whenever there is 2 cm or more of water in the vault (Figure 2). Based on the surface area of each 55-gallon drum, this is 117mL/min per mesocosm (Taylor et al. 2016). A float switch located inside the vault will trigger the pumps (Figure 3). A flow totalizer on the pump inlet will confirm that desired flow rates are being achieved and measure the total quantity of stormwater dosed. Flow will be continuously monitored at the pump inlet throughout the project period.

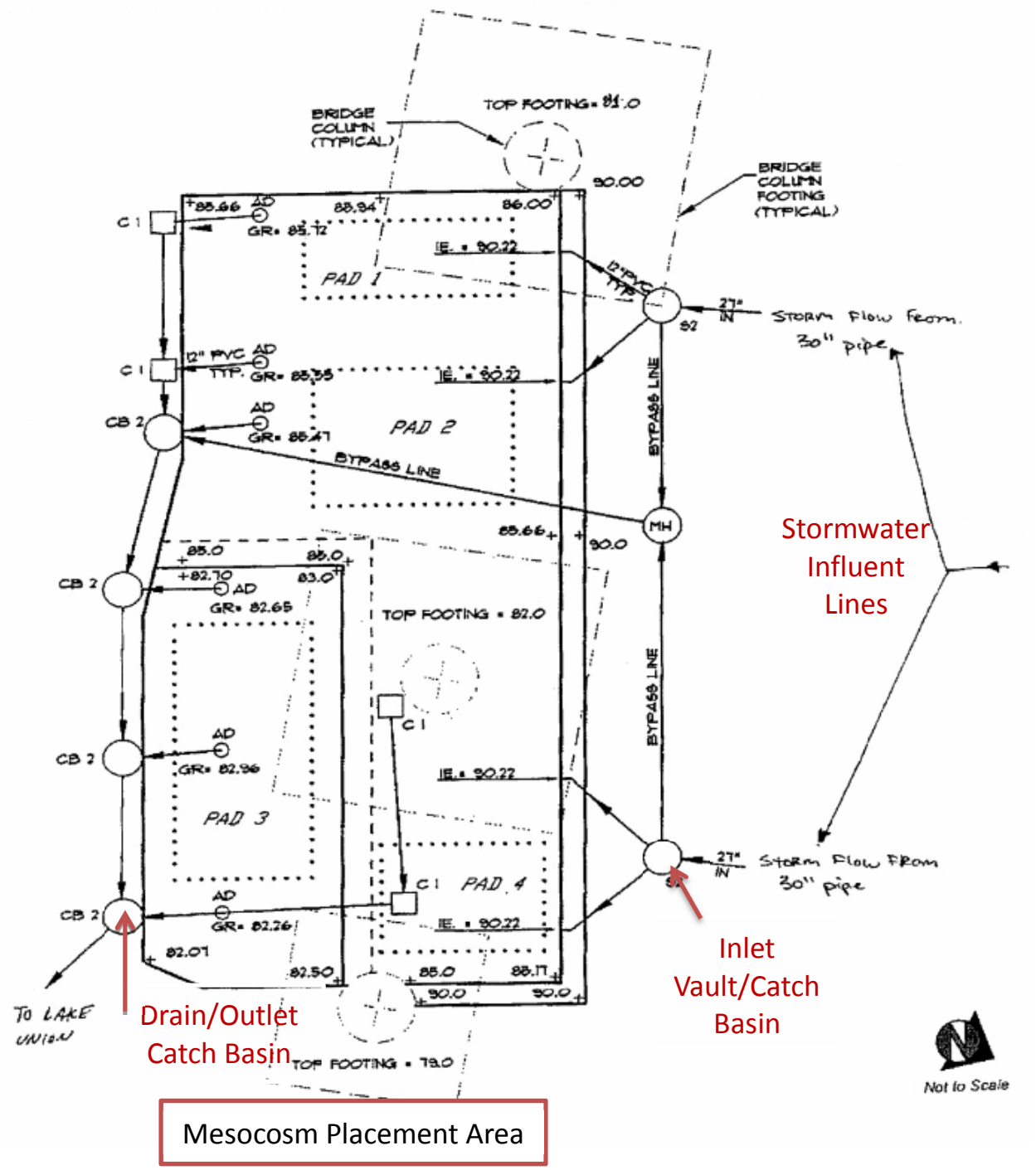

Figure 1. Layout of WSDOT Ship Canal Stormwater Research Facility with vault inlet-drain lines shown. See Figure 3 for pump piping

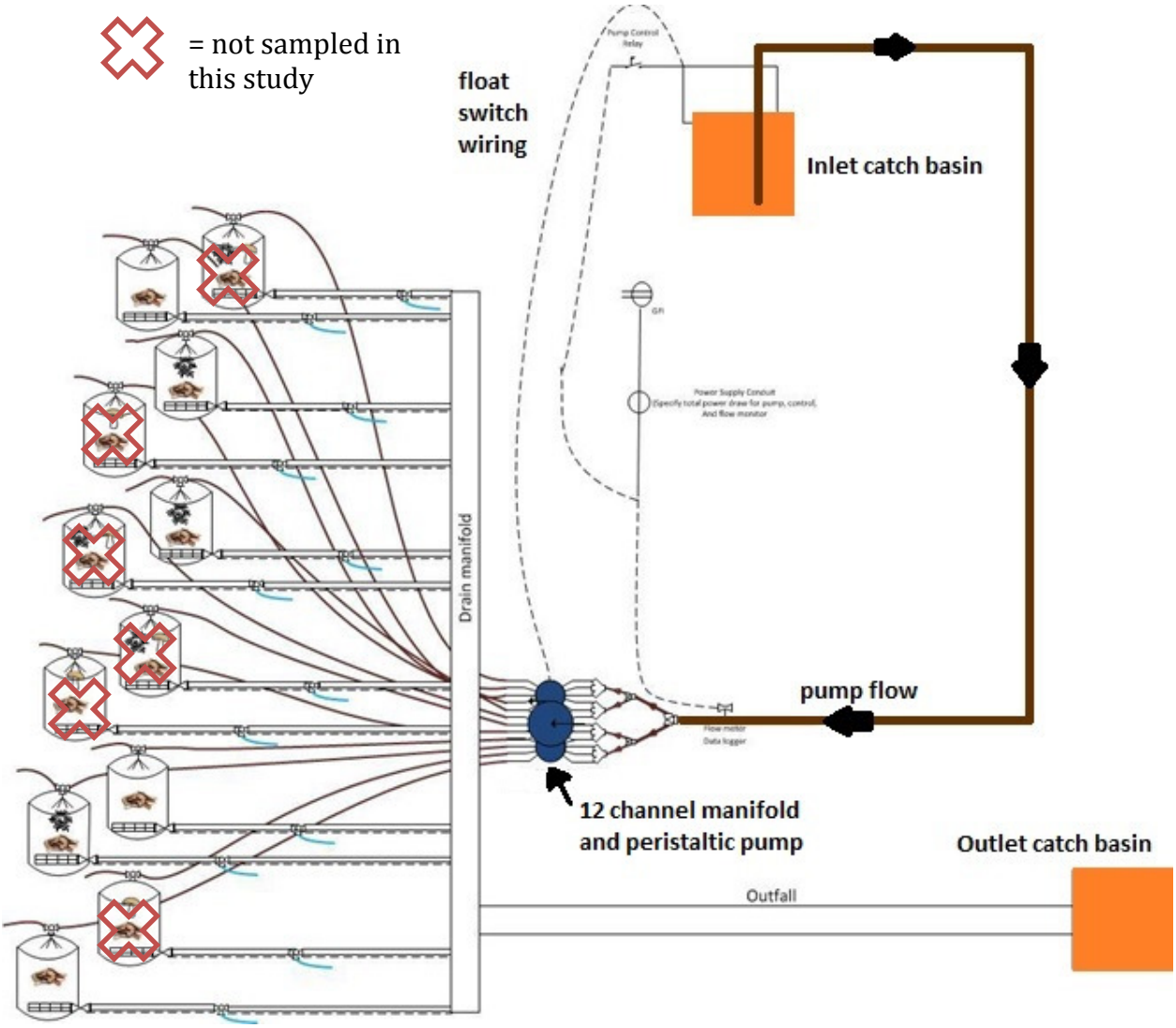

Figure 2. Schematic of Mesocosm Placement Area; mesocosms not sampled during this study are part of the Taylor et al. (2016) study.

2.0 PROJECT OBJECTIVES

This study will evaluate PCB sequestration in mesocosms which are designed to represent bioretention BMPs. The ultimate objective is to develop a better understanding of how well BSM captures and retains PCBs across seasons over a two-year period.

The project will address the following specific questions using the data analysis tools noted:

1. What is the PCB removal (capture) rate in BSM, and does it vary by congener?
    a. Evaluated by comparison of paired influent and effluent PCB concentrations (both as total PCBs and individual congeners) measured during storm events.
    b. Evaluate removal differences with and without plants.
2. What is the wet season PCB sequestration (retention over multiple storm events) in BSM, and does this vary by congener?
    a. Evaluated by comparison of PCB soil concentrations at the beginning of the wet season (October) relative to end of the wet season concentrations (May).
    b. Evaluate sequestration differences with and without plants.
    c. Compare sequestered mass of PCBs with estimated stormwater loads.
3. What is the PCB retention in BSM during the dry season, and does it vary by congener?
    a. Evaluated by comparisons of PCB soil concentrations at the beginning of the dry season (May) relative to end of the dry season concentrations (October).
    b. Evaluate removal differences with and without plants.

3.0 PROJECT DESCRIPTION

The study will be conducted in conjunction with the WSU/USFWS bioretention performance project (Taylor et al. 2016) using mesocosms to evaluate the influence of plants and fungi on nutrient, metal, and polycyclic aromatic hydrocarbon (PAH) removal rates (four treatment types total[1]). Stormwater, from a downspout draining from Interstate-5 (I-5), will be dispersed to mesocosms constructed in 55-gallon barrels. For the purposes of this study, only two of WSU/USFWS's four mesocosm types will be tested:

1. BSM only, and
2. BSM with plants

The influent, effluent, and BSM from the two treatments will be analyzed for PCB congeners. Three replicate mesocosms for each treatment type will be used (a total of six mesocosms). Results will be used to calculate a PCB mass balance in the mesocosms over a two-year period. The mass balance information will answer these questions:

1. What fraction of the PCBs entering the mesocosm from stormwater is sequestered into BSM? and,
2. To what extent is this PCB removal permanent or seasonal?

Answering these questions will help estimate both seasonal losses of PCBs from BSM and the lifetime PCB accumulation in a bioretention cell.

Sampling will be conducted quarterly during eight storm events over a two-year period. An influent sample and field replicate will be collected during each event for a total of 16 influent samples. Effluent samples will be collected at the same time from each of the mesocosm replicates. One effluent field replicate will be collected during each sampling event. With three mesocosms per treatment, eight quarterly events, and one effluent replicate per event, this is a total of 56 effluent samples. Prior to initiation of sampling, one pump system field blank[2] will be analyzed using laboratory supplied deionized water. No effluent field blank will be collected. A summary of the type and number of influent and effluent samples to be collected is presented in Table 1.

[1] The four total treatment types are BSM only, BSM with plants, BSM with fungi and no plants, BSM with plants and fungi.

[2] Deionized laboratory water will be pumped from supply jars through all inlet piping, the 12 channel manifold, peristaltic tubing, and distribution tubing to a new proofed clean sampling jar.

Table 1. Sample types collected by project quarter

Sample type	Analysis	Number of Samples per Project Quarter								Total Samples
		1*	2	3	4	5	6	7	8	
Influent	PCB, TOC, DOC, TSS	1 + 1 rep	1 + 1 rep	1 + 1 rep	1 + 1 rep	1 + 1 rep	1 + 1 rep	1 + 1 rep	1 + 1 rep	16
Field Blank (water)	PCB, TOC, DOC, TSS	1								1
Effluent	PCB, TOC, DOC, TSS	6 + 1 rep	6 + 1 rep	6 + 1 rep	6 + 1 rep	6 + 1 rep	6 + 1 rep	6 + 1 rep	6 + 1 rep	56
BSM Soils	PCB	6 + 1 rep	6 + 1 rep	6 + 1 rep	6 + 1 rep	6 + 1 rep	6 + 1 rep	6 + 1 rep	6 + 1 rep	56
									Total	129

*Anticipated starting quarter is Oct-Dec 2016

Bioretention soil mix samples will be collected quarterly for two years; BSM samples will not be collected during storm events. Samples will be collected from the entire 18-inch soil column, excluding the gravel underdrain portions, using a small (10 mm-diameter) stainless steel tube driven into the soil (Haglof Soiltax model soil sampler). Each BSM sample will be composited from at least two tube insertions. Any holes remaining will be backfilled with BSM to ensure that preferential flow pathways are not created. One field replicate per treatment type will be collected each quarter. A summary of the number and type of mesocosm soil samples to be collected is presented above in Table 1.

3.1 Study Area

The bioretention mesocosms will be located at the Washington State Department of Transportation (WSDOT) "Lake Union Ship Canal Research Facility," located at 650 NE 40th St., Seattle WA (Figure 1) underneath the north end of the I-5 Ship Canal Bridge. The mesocosms will receive runoff from a 12.8 hectare (31.6 acres) drainage area including 9.2 hectares (22.7 acres) of I-5 pavement and 3.6 hectares (8.9 acres) of roadside landscaping. I-5 through Seattle is a major transportation corridor with approximately 250,000 vehicles per weekday using the Ship Canal Bridge.

Figure 3. Study Area Location in Seattle, Washington

3.2 Contaminants of Interest

Urban stormwater typically contains a wide range of pollutants including nutrients, bacteria, metals, and various organic contaminants (Hobbs et al. 2015). However, this study is focused on PCB behavior in bioretention BMPs. All samples will be analyzed for

PCB congeners. Total suspended solids (TSS), total organic carbon (TOC), and dissolved organic carbon (DOC) will also be analyzed in the stormwater influent and effluent. These parameters may help explain the behavior of the PCBs. Measurement of TSS, TOC and DOC will be conducted by the WSU/USFWS contract laboratory. The measurement quality objectives for these parameters are covered in the WSU/USFWS QAPP (Taylor et al. 2016)

4.0 ORGANIZATION AND SCHEDULE

The project team consists of personnel from King County's Water and Land Resources Division (WLR Division), WSU and USFWS representatives, a RSMP coordinator from Ecology, and an RSMP runoff program manager from WSDOT (Table 2). Pacific Rim Laboratories will conduct PCB congener analysis, and a contracted validator will conduct PCB congener data validation.

King County WLR Division, Science Section

- Richard Jack – Project Manager, lead investigator
- Jenée Colton – Technical Assistance
- Carly Greyell – Technical Assistance
- Deborah Lester – Toxicology and Contaminant Assessment Unit (TCA) Supervisor

This group is responsible for project planning, communicating between involved parties, soil sampling, and validating, synthesizing, and communicating results.

King County WLR Division, King County Environmental Lab

- Fritz Grothkopp – Laboratory Project Manager (LPM)
- Colin Elliott – Quality Assurance Officer

This group is responsible for shipping samples to Pacific Rim for PCB analysis, submitting data to the independent data validation chemists, and delivery of validated data to the project manager.

WSU/USFWS Representatives

- Alex Taylor – WSU Graduate Student
- Jay Davis – USFWS Lead Investigator
- Jenifer McIntyre – WSU Principle Investigator

This group is responsible for construction of the mesocosms, periodic maintenance, and collection of stormwater influent and effluent samples in cooperation with King County WLR.

RSMP Representatives

- Brandi Lubliner, Ecology – RSMP Coordinator
- Alex Nguyen, WSDOT – Highway Runoff program Manager

This group is responsible for providing coordination between the SWG and the rest of the project team, as well as technical oversight. A technical liaison has not been named yet.

Table 2. Team Member Contact Information

Organization	Name	Contact Information
King County	Richard Jack	206-477-4715; richard.jack@kingcounty.gov
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WSU	Jenifer McIntyre	206-445-4650; jen.mcintyre@wsu.edu
Ecology	Brandi Lubliner	360-407-7140; brandi.lubliner@ecy.wa.gov
WSDOT	Alex Nguyen	206-440-4537; nguyeal@wsdot.wa.gov
Pacific Rim Laboratories	David Hope	604-532-8711; dave@pacificrimlabs.com

Table 3 details the project schedule and deliverable due dates.

Table 3. Schedule of Tasks

Activity	Anticipated Initiation Date	Anticipated Completion Date	Deliverable	Deliverable Due Date
TASK 2.0 – Water and soil sampling and analysis				
Storm Sampling (8 quarterly storm events)	Nov. 2016	June 2018	Documenting Progress Reports	Semi-annually
Soil Sampling (8 quarterly sampling events)	Nov. 2016	June 2018	Documenting Progress Reports	Semi-annually
Analysis at Pacific Rim Laboratories	Dec. 2016	July 2018	Documenting Progress Reports	Semi-annually
TASK 3.0 – Data validation, compilation, and database				
Data validation	Jan. 2017	August 2018	Documenting Progress Reports	Semi-annually
Database	Jan. 2017	July-August 2018	Documenting Progress Reports	Semi-annually
TASK 4.0 – Conceptual model, draft and final report				
Draft Report	Sept. 2018	Oct. 2018	Draft Report	Nov 2018
Final Report	Nov. 2018	Jan. 2019	Final Report	Jan 2019

Activity	Anticipated Initiation Date	Anticipated Completion Date	Deliverable	Deliverable Due Date
TASK 5.0 – Outreach and communication				
Website describing project goals and deliverables	Jan. 2017	Jan. 2019	1. Post QAPP 2. Post Final Report	Nov. 2016 Jan. 2019
Submit system data to National BMP database	Nov. 2018	Dec. 2018	Data submitted	Dec. 2018
Presentation to permittees	Sept. 2018	Dec. 2018	Copy of presentation	Dec. 2018
TASK 6.0 – Project Management				
Project management	Nov. 2016	Dec. 2018	Documenting Progress Reports	Semi-annually

5.0 QUALITY OBJECTIVES

The data quality objectives (DQOs) for this effort are to collect data of known and sufficient quality to meet study goals. The data quality indicators of precision, bias, sensitivity and accuracy are described within this section, while representativeness, comparability, completeness are described in Section 6, after the details of the sampling design. Detailed descriptions and specific limits for quality assurance/quality control (QA/QC) samples are discussed in Section 9.

5.1 Precision

Precision is the agreement of a set of results among themselves and is a measure of the ability to reproduce a result. For this project, evaluation of precision will be based on field replicates, laboratory duplicates or triplicates and matrix spike duplicates. The QA/QC criteria presented in Section 9 shall be met for precision. Should criteria not be met, data will be flagged accordingly and conclusions qualified.

5.2 Bias

Bias is a measure of the difference, due to a systematic factor, between an analytical result and the true value of an analyte. Bias will be evaluated by analyzing field blanks, method blanks, spike blanks, matrix spikes, certified reference materials, laboratory control samples and/or surrogates, along with ongoing recovery sample control charts. Results for these QA/QC samples must be within the criteria presented in Section 9.

5.3 Sensitivity

Sensitivity is a measure of the capability of analytical methods to meet the study goal. The analytical method being used for PCB congeners is a rigorous, low-level method for water samples. The analytical method detection limits (MDLs) presented in Section 8 are sensitive enough to detect low level PCB congeners at concentrations sufficient to increase the understanding of the effect of bioretention treatments on concentrations and loadings.

While PCBs have not previously been analyzed in effluent from Washington bioretention BMPs receiving highway runoff, it is expected that many congeners will be detected in influent and soil samples based on comparable data from the I-90 Bridge (King County 2013). Fewer congeners are expected to be detected in effluent samples, but this should not limit the study's ability to describe PCB behavior in the bioretention mesocosms during individual storms and multiple seasons

5.4 Accuracy

Accuracy is an estimate of the difference between the true value and the measured value. The accuracy of a result is affected by both systematic and random errors. Accuracy of the pump rate will be verified by checking the flow rate by measuring the output over 5

minutes with a stopwatch and volumetric flask during storm event sampling. Flow rate checks will occur at least quarterly. Total flow measurements will also be reviewed (Section 7.1).

Accuracy of the analytical results will be evaluated using field blanks, method blanks, and/or laboratory control samples, along with ongoing recovery sample control charts. Results for the analytical QA/QC samples must be within the criteria presented in Section 9. Additionally, the isotopic dilution method for PCBs is the most rigorous method for congener analysis and uses isotopically labeled congeners, to track recovery performance of the range of congeners. Thus, each congener concentration is theoretically adjusted for the extraction efficiency and analytical performance of that specific sample.

6.0 SAMPLING DESIGN

The goal of this study is to evaluate the effectiveness of bioretention to remove and sequester PCBs from stormwater on both an individual storm and seasonal basis. The following sections describe the sampling design to achieve the study objectives described above in Section 2.

6.1 Site Description

Twelve bioretention mesocosms will be located at the WSDOT "Lake Union Ship Canal Research Facility," underneath the north end of the Ship Canal Bridge (Figure 1). Only six of the mesocosms will be used for this study: three with BSM only, and three with BSM and plants. The remaining mesocosms are for the companion WSU/USFWS study investigating the influence of fungi on BSM.

The site is gated and secured with a six-foot-tall chain link and barbed wire fence. The mesocosms will be receiving runoff from a 12.8 hectare (31.6 acres) drainage area including 9.2 hectares (22.7 acres) of pavement and 3.6 hectares (8.9 acres) of roadside landscaping. Stormwater drains from the roadway and roadside areas into a large (1.5m x 1.5m) concrete flow splitting vault (Figure 2) before being gravity fed to other existing test facility catch basins and structures. The stormwater vault is partially below ground; therefore, it will be necessary to pump the influent from the vault to the mesocosms.

6.2 Qualifying Storm Event Criteria for Sampling

One challenging aspect of stormwater sampling is storm variability. The pump will be float-triggered to dose the mesocosms continuously whenever stormwater is present in the supply vault above the switch. The float switch will be set as low as practical within the vault which is approximately 2 cm above the bottom. This depth is also the minimum water depth necessary to ensure that air is not entrained into the inlet.

Influent and effluent storm samples will only be collected during rain event conditions as defined below. The sampling criteria presented below have been adapted from the Technology Assessment Protocol – Ecology (TAPE) *Guidance for Evaluating Emerging Stormwater Treatment Technologies* (Ecology 2011).

Storm Event Conditions to Trigger Effluent/Influent Sampling:

- At least 0.15 inches of rainfall, no fixed maximum
- A minimum one hour storm duration, no fixed maximum
- No antecedent dry period required
- Effluent must be flowing through vault

There are no other conditions on the quarterly influent and effluent sample collection and any storm meeting these goals during the quarter may be sampled. The sampling criteria described here are less rigorous than those for the Taylor et al. (2016) companion study, but because samples will typically be collected concurrently, those storm guidelines will likely dictate the storms sampled for this study. The Seattle Rain Watch program (http://atmos.washington.edu/SPU/) is the primary source for storm information for this project. Additional weather and storm information is provided in Taylor et al. (2016). To the extent possible, influent and effluent samples will be collected during storms of varying intensity to represent a variety of conditions.

6.3 Measured Parameters

PCB congeners will be analyzed by Pacific Rim Laboratories. The following conventional parameters will be analyzed by the WSU contracted laboratory (Taylor et al. 2016) for each stormwater influent and effluent sample:

- Total suspended solids
- Total organic carbon
- Dissolved organic carbon.

6.4 Representativeness

Representativeness expresses the degree to which sample data accurately and precisely represent a characteristic of a population, parameter variations at the sampling point, or an environmental condition. Samples are to be collected in such a manner as to minimize potential contamination and chemical degradation in the water and soils. This can be achieved by following guidelines for sample carboy decontamination, sample acceptability criteria, sample processing, observing proper hold-times, preservation, and sample storage, as described in Sections 7 and 9. In order to reduce the risk of cross-contamination between mesocosms, all tubing (sampling and sample splitting tubing) will be pre-cleaned and either new or dedicated to a particular mesocosm, as described in Sections 7.2 and 7.3. In order to better estimate average PCB concentrations in influent and effluent samples, a range of storm intensities will be targeted. The samples are intended to generate data of sufficient quality to allow analysis of treatment effectiveness and seasonal retention of both total PCBs and individual PCB congeners.

6.5 Comparability

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another. Comparability is addressed through use of standard techniques to collect and analyze representative samples, along with standardized data verification and reporting procedures described in this QAPP. Changes or updates to analytical methods and sampling techniques midway into the project must be tested, validated, and shown to be equivalent to existing methods. This validation must be approved by the project manager and QA officers before being implemented.

The mesocosms tested here are intended to represent an Ecology-approved stormwater treatment BMP incorporated into an urban highway retrofit project. Although every retrofit project is unique due to site considerations, this project will provide transferable information in the form of (1) PCB removal and retention performance of a common treatment feature installed under western Washington geological and climate conditions in an area of high impervious surface, and (2) the collective PCB performance of this treatment feature and on both stormwater and soil quality over a two year period.

To ensure study findings are relevant to regional needs, the BMP design and sample analysis should be comparable to those used in other jurisdictions. This will be achieved by using Ecology-specified BSM to a depth of 18 inches with and without plants. Under the BSM a gravel layer with an underdrain will mimic a full-scale bioretention BMP (T7.30 as designed in Ecology's SMMWW). The influent and effluent collection methods and reporting limits used in this study are comparable to the 2011 TAPE protocol, except that approximately 75-minute time-weighted influent and effluent composites will be collected instead of TAPE specified flow-weighted composites. The number of storm samples collected in this study will not provide the statistical power achievable through the TAPE protocols. However, given the variability in highway stormwater PCB concentrations (King County 2013) it is not cost effective to provide this power for this effort. All sample containers, preservation methods and holding times, and analytical methods are comparable or more stringent than those required by the 2011 TAPE protocol.

6.6 Completeness

Completeness is defined as the total number of samples analyzed for which acceptable analytical data are generated, compared to the total number of samples submitted for analysis. Sampling according to storm criteria, along with adherence to standardized sampling and testing protocols outlined in this QAPP, will aid in providing a complete set of data for this project. The goal is the collection of samples during eight storm events, which is 100% completeness. BSM sample collection methods may be adapted or modified if collecting the required number samples by push probe is problematic. If completeness goals are not achieved, the project team will evaluate if the DQOs can still be met or if additional samples may be needed.

7.0 SAMPLING AND MONITORING PROCEDURES

Sample collection and flow monitoring procedures are presented here. The following sections also describe additional sampling considerations, equipment, sampling initiation, sample handling, decontamination procedures, collection of QA/QC samples, and preventative maintenance.

7.1 Pump Rate and Flow Meter Installation and Confirmation

Two Masterflex peristaltic pumps (L/S model with variable speed using a combined 4 and a 2 channel head) will be wired in series with a float switch. The in-series wiring will prevent both pumps from operating should an electrical failure occur in either pump. The two pumps will draw water from a common inlet and simultaneously provide 117mL/min of stormwater influent to all mesocosms. The flow rate will be confirmed before initiation of sampling by timing the rate laboratory grade water is pumped through the tubing during the collection of a blank sample. Flow rate will also be confirmed when stormwater influent and effluent samples are collected by recording the volume of influent pumped over a set period of time into a volumetric flask.

Total flow data will be downloaded from the flow totalizer (Cole Palmer model EW-32615-62) at least monthly and whenever storm influents and effluents are collected. Because the flow meter will be attached to the single inlet tube leading to the 12 channel pumps (Figure 3), total flow divided by 12 is the volume dosed to each mesocosm since the last download. Total flow (liters) will be compared with the total runtime (minutes) to double check that each of the 12 legs of the pump manifold have been dosing at 117mL/min.

7.2 Sample Collection – Influent and Effluent

The pump distribution system (Figure 3) is below the vault inlet. This means that once the pump has actuated and primed the inlet tubing, influent will potentially siphon from the vault. The peristaltic pump will prevent more than 117mL/min from dosing each mesocosm, but the siphon will be used to collect influent samples by installing a diverter tap before the pump manifold. This study will collect approximately 300mL of influent from the inlet diverter tap at time zero (minutes), time 25, and time 50 (Taylor et al. 2016). Taylor et al. (2016) describes the time-paced water sampling in greater detail, although they are collecting influent samples from different points than this study. This study will collect two 900-1,000 mL influent samples from the diverter tap during each event to allow for archiving extra influent samples and required field and laboratory duplicates.

Taylor et al. (2016) describes the effluent composite sampling protocol in detail. Briefly this involves collecting 2,340 mL aliquots of effluent from each mesocosm's underdrain

with glass carboys. Three aliquots are to be collected total, one from 5 to 25 minutes, one from 30 to 50 minutes, and on from 55 to 75 minutes. All three aliquots are collected into the same glass carboy. These carboys will be iced and brought back the laboratory for splitting. A magnetic stir bar will continuously agitate the carboys will the required sample jars are filled using a Teflon siphon tube. Two 1L effluent samples will be collected per mesocosm to provide sufficient effluent for archiving and required field and laboratory duplicates.

7.3 Sample Collection – Soils

Mesocosm soils will be collected quarterly over a two-year period using a narrow 10mm diameter stainless steel soil corer (Haglöf Soiltax brand). The corer will be inserted the full depth (approximately 18 inches) of BSM to collect each sample and any holes remaining will be backfilled with BSM. The core will be homogenized in a stainless steel bowl using a pre-cleaned spoon that was wrapped in aluminum foil then transferred to the proofed clean glass sampling jars.

7.4 Sampling Initiation

7.4.1 Monitoring Forecast

Although it is ideal to randomize sampling days, this is unrealistic for the personnel resources. Alternatively, the project manager and field team will plan sampling events around the weather forecast and available personnel. When a qualifying storm is forecast (as defined in Section 6.2), field personnel will prepare for the upcoming event after a discussion with the project manager.

7.4.2 Sampling Initiation Procedures

Once the decision is made to initiate sampling, the field staff will gather all materials for deployment, which may include decontaminated containers, and ice, and proceed to sampling sites. When collecting or handling sample containers, field personnel will wear powder-free nitrile gloves for safe handling to prevent cross contamination of samples.

7.5 Installation Considerations

Sampling inlet tube and float switch in the vault may require entering this confined space. This will be done by personnel who have the training and experience to safely enter these spaces.

7.6 Additional Field Equipment

Sampling and safety supplies include the following:

- Pre-cleaned stainless steel bowls and spoons
- Ziploc® bags

- Cooler with ice
- Nitrile gloves
- Field notebook
- Sample labels
- Chain-of-custody forms
- Camera
- Hard hats
- Safety vests
- Safety shoes
- Safety glasses

When visiting the sampling site, field personnel will record the following information on field forms that are maintained in a waterproof field notebook:

- Date and time of sample collection/visit
- Name(s) of sampling personnel
- Weather conditions
- Number and type of samples collected
- Pump flow check procedures
- Sequence of events (order of sites sampled)
- Time of flow data download
- Log of photographs taken[3]
- Comments on the working condition of the sampling equipment
- Deviations from sampling procedures
- Unusual conditions (e.g., water color or turbidity, presence of oil sheen, odors, and land disturbances)

7.7 Sample Handling Procedures

7.7.1 Sample Delivery and Storage

After sampling is completed, all samples will be stored on ice. Water sample carboys will be transported back to WSU-Puyallup for splitting into sample containers. Soil samples will be transported back to KCEL for storage until ready for shipment to the analytical laboratory. Water samples will be transported from WSU-Puyallup to KCEL on ice and/or ice packs.

[3] At a minimum, photos should document the mesocosms, pump outlets, and plant status. Any deviations from the QAPP or unusual conditions must also be photographed.

Containers for PCB congener analysis will be delivered to Pacific Rim Laboratories within one to three months of sample collection. Samples will be held at KCEL at 4 degrees C in darkness until shipping. Samples will either be driven to Pacific Rim Laboratories or shipped via overnight express delivery service.

Table 4 shows sample handling and storage requirements for PCB congeners in soil and water. Sample handling, preservation, and storage requirements for TOC, DOC, and TSS are shown in Table 6 of Taylor et al. (2016).

Table 4. Parameter List with Sample Volume, Container, Preservation, Storage, and Holding Time Requirements

PCB Congeners	Container	Storage Prior to Preservation	Preservation Holding Time	Preservation Technique	Analysis Holding Time
Water	2 1-L amber glass	Cool to ≤4 ° C	NA	Cool to ≤4 ° C in the dark	1 year
Soil	8 oz wide mouth glass	Cool to ≤4 ° C	NA	Cool to ≤4 ° C in the dark	1 year

7.7.2 Chain of Custody

Chain of custody (COC) will commence at the time the mesocosms are constructed and installed. Mesocosms and the associated stormwater dosing pumps will be secured behind a locked chain link and barbed wire fence to ensure no tampering occurs. Thus, all samples will be under direct possession and control of WSU or King County field personnel. For COC purposes, closed/latched storm drains, fenced areas, and field vehicles will be considered "controlled areas." All sample information will be recorded on a COC form, an example of which is included as Appendix B. This form will be completed in the field and will accompany all samples during transport and final delivery to KCEL. Upon arrival at KCEL, the samples will be preserved as needed, then logged into the laboratory data management system and stored in a secure refrigerator. The date and time of sample delivery will be recorded and the COC form will be signed off in the appropriate sections at this time. Once completed, original COC forms will be archived in the project file.

Samples delivered after regular business hours will be split as needed and stored in a secure refrigerator until the next day. Samples delivered to the contract laboratory, Pacific Rim Laboratories, will be accompanied by a properly-completed KCEL COC form and custody seals will be placed on the shipping cooler. Pacific Rim Laboratories will be expected to provide a copy of the completed COC form as part of their analytical data package.

7.7.3 Sample Documentation

Sampling information and sample metadata will be documented using the methods described below:

- Field sheets generated by King County's Laboratory Information Management System (LIMS) will be used at all stations and will include the following information:
    1. Sample ID number
    2. Locator/station name
    3. In-vault water depth at initiation and termination of sample collection.
    4. Date and time of sample collection (start and end times of the compositing period)
    5. Initials of all sampling personnel

- LIMS-generated container labels will identify each container with a unique sample number, station and site names, collect date, analyses required, and preservation method.
- The field sheet will contain records of collection times, general weather, and the names of field crew.
- COC documentation will consist of the Lab's standard COC form, which is used to track release and receipt of each sample from collection to arrival at the lab.

7.8 Decontamination Procedures

Before mesocosms are dosed, all equipment in contact with influents or effluents will be decontaminated. Carboys and their associated Teflon® tubing shall be cleaned with: (1) Alconox® or other suitable laboratory detergent; (2) a sulfuric acid rinse; (3) a deionized water rinse; and only for non-tubing surfaces, (4) an acetone rinse. In a previous study, it was determined that acetone lingering in autosampler tubing can interfere with TOC and DOC analysis (King County 2014b); therefore, tubing will not be rinsed with acetone. All tubing, fittings, and connectors are either nylon, Teflon®, or platinum-cured silicon[4] and are to be cleaned in the same manner. Composite sample bottles tubing will be cleaned prior to each sampling event. Acetone solvent rinses shall be used for carboys per Environmental Protection Agency (EPA) methods 1668C and 1613.

The soil corer, homogenization bowls, and spoons will be precleaned according to steps 1 through 4 above. After air drying, equipment will be wrapped in aluminum foil until use in the field.

Proofed clean PCB sampling containers will be supplied by the contract laboratory. Proper personal protective equipment (new powder-free gloves for each site) should be worn during sampling activities and during decontamination processes.

7.9 Collection of QA/QC Samples

Table 5 summarizes the QA/QC samples to be collected to satisfy project objectives.

Table 5. QA/QC Samples Required

QA/QC Sample Type	Number of QA/QC Samples	Collection Procedure
Equipment Blank	One for pump delivery setup	Run ASTM Type I or II de-ionized water supplied by Pacific Rim Laboratory through the pump, tubing, and distribution manifold after decontamination and collect sample in the appropriate container. Place immediately on ice.
	No soil equipment blank	

[4] Previous studies have indicated silicone tubing, used for peristaltic pumps, may be a source of PCBs (King County, unpublished data) .

QA/QC Sample Type	Number of QA/QC Samples	Collection Procedure
Field Replicates	One influent per storm event **(8 total)**	Collect one replicate sample per event from the same 7L carboy used to create the primary sample.
	One effluent per storm event **(8 total)**	Collect one replicate sample per event from one of the 7L carboys used to create the primary samples. Rotate replicate collection between the 6 treatment mesocosms so replicate samples are collected no more than twice from each mesocosm.
	Soil **(8 total)**	Collect one replicate sample from one of the 6 mesocosms per sampling event. Rotate replicate collection between the 6 treatment mesocosms so replicate samples are collected no more than twice from each mesocosm.

7.10 Periodic Preventative Maintenance

Periodic preventative equipment maintenance will occur as needed between storm events to ensure pump and flow meter equipment is operating properly. This will include confirming float actuator function, ensuring the pump, distribution manifold, and flow meter are not leaking, confirming pump rate, downloading flow data, and to check for debris that could interfere with readings. 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 will be documented in the final report under Deviations from the QAPP.

8.0 MEASUREMENT PROCEDURES

WSU will be measuring TOC, DOC, and TSS as part of a companion study. Taylor et al. (2016) describes these methods and the applicable MDLs, and the data will be shared and used in this project. This study will collect and analyze influent, effluent and bioretention mesocosm soils for PCB congeners.

8.1 PCB Congener Analytical Methods and Detection Limits

PCB congeners will be analyzed following EPA Method 1668 Revision C (EPA 2010a), which is a high-resolution gas chromatography/high-resolution mass spectroscopy (HRGC/HRMS) method using an isotope dilution internal standard quantification. Method and reporting detection limits are not applicable for this method because limits of sample quantitation are derived from calibration capabilities and ubiquitous, but typically low level, equipment and laboratory blank contamination. Additional reporting limit terms used particularly for PCB congener analyses are "sample specific detection limits" and "lowest method calibration limits". The sample specific detection limit (SDL) is determined by converting the area equivalent to 2.5 times the estimated chromatographic noise height to a concentration. For each sample analysis run, SDLs are determined for each individual congener and account for any effect of matrix on the detection system and recovery achieved through the analytical work-up. Lowest method calibration limits (LMCL), also called estimated quantitation limits (EQL), are based on calibration points from standard solutions. They are prorated by sample size and are supported by statistically derived method reporting limit (MRL) values.

The PCB congener data will be reported to LMCLs and flagged down to the SDL value. In many cases the SDL may be below the LMCL. Method 1668C defines a Minimum Level (ML) value for each congener. The ML value is used to evaluate levels in the method blank. The ML is based on the LMCL and any laboratory performing the method should be able to achieve at least that level. Pacific Rim Laboratories uses an additional calibration point that is lower than the calibration points specified in the method; as such they are able to quantify congeners below the ML specified in the method.

Pacific Rim Laboratories will perform this analysis according to their SOP LAB02. A one-liter sample will be extracted followed by standard method cleanup, which includes an acid wash followed by Acid Silica and Alumina column chromatography. Analysis is performed with an SGE HT-8 column. Method 1668C requires that if a sample contains more than 1% total solids, the solids and liquid will be extracted and analyzed separately.

Table 6 lists the 209 PCB congeners and typical SDL and EQL (lower calibration limit) values for waters and soils. The reporting limits for individual samples may differ from those in Table 5 since they are determined by signal to noise rations and changes to final

volumes. Note that several of the congeners co-elute and a single SDL or EQL value is provided for the congeners in aggregate.

Table 6. Soil and Water Detection Limits for PCB Congeners

Analyte	PCB	Soil			Water	
		MDL	EQL		MDL	EQL
		ng/kg			pg/L	
2-MoCB	PCB-1	0.6	4		6.0	10
4-MoCB	PCB-3	1.2	4		6.1	10
2,2'-DiCB	PCB-4	2.2	4		6.5	10
2,4'-DiCB	PCB-8	2.8	4		10	10
2,6-DiCB	PCB-10	2.2	4		7.5	10
4,4'-DiCB	PCB-15	2.1	4		3.6	10
2,2',5-TrCB	PCB-18	1.2	4		1.8	10
2,2',6-TrCB	PCB-19	1.0	4		9	10
2,3,4'-TrCB	PCB-22	0.9	4		12	10
2,4,4'-TrCB	PCB-28	0.9	4		4.7	10
2',3,4'-TrCB	PCB-33	0.8	4		2.5	10
3,4,4'-TrCB	PCB-37	1.3	4		2.1	10
2,2',3,3'-TeCB	PCB-40	2.0	4		1.8	10
2,2',3,4-TeCB	PCB-41	2.4	4		5.8	10
2,2',3,5-TeCB	PCB-44	1.3	4		3.9	10
2,2',4,5'-TeCB	PCB-49	2.0	4		3.2	10
2,2',5,5'-TeCB	PCB-52	1.3	4		2.7	10
2,2',6,6'-TeCB	PCB-54	0.9	4		1.4	10
2,3,4,4'-TeCB	PCB-60	1.6	4		1.9	10
2,3',4,4'-TeCB	PCB-66	2.2	4		3.6	10
2,3',4',5-TeCB	PCB-70	2.2	4		2.3	10
2,4,4',5-TeCB	PCB-74	1.3	4		2.3	10
3,3',4,4'-TeCB	PCB-77	0.13	4		1.2	10
3,4,4',5-TeCB	PCB-81	0.06	4		0.76	10
2,2',3,4,5'-PeCB	PCB-87	1.6	4		3.6	10
2,2',3,4',5-PeCB	PCB-90	2.0	4		12.9	10
2,2',3,5',6-PeCB	PCB-95	0.9	4		6.0	10
2,2',4,4',5-PeCB	PCB-99	2.3	4		5.4	10
2,2',4,5,5'-PeCB	PCB-101	1.4	4		3.7	10
2,2',4,6,6'-PeCB	PCB-104	0.5	4		2.4	10
2,3,3',4,4'-PeCB	PCB-105	0.12	4		5.7	10
2,3,3',4',6'-PeCB	PCB-110	1.0	4		6.2	10
2,3,4,4',5-PeCB	PCB-114	0.09	4		1.5	10
2,3',4,4',5-PeCB	PCB-118	0.19	4		2.9	10
2,3',4,4',6-PeCB	PCB-119	0.7	4		1.3	10

Analyte	PCB	Soil			Water	
		MDL	EQL		MDL	EQL
		ng/kg			pg/L	
2',3,4,4',5-PeCB	PCB-123	0.13	4		1.9	10
3,3',4,4',5-PeCB	PCB-126	0.10	4		1.4	10
2,2',3,3',4,4'-HxCB	PCB-128	0.6	4		2.9	10
2,2',3,3',4,5-HxCB	PCB-129	1.5	4		9.0	10
2,2',3,4,4',5-HxCB	PCB-137	1.1	4		13	10
2,2',3,4,4',5'-HxCB	PCB-138	1.6	4		2.0	10
2,2',3,4,5,5'-HxCB	PCB-141	0.9	4		8.0	10
2,2',3,4,5',6-HxCB	PCB-149	1.0	4		1.4	10
2,2',3,5,5',6-HxCB	PCB-151	1.4	4		1.2	10
2,2',4,4',5,5'-HxCB	PCB-153	0.9	4		4.1	10
2,2',4,4',6,6'-HxCB	PCB-155	0.8	4		2.2	10
2,3,3',4,4',5-HxCB	PCB-156	0.07	4		1.5	10
2,3,3',4,4',5'-HxCB	PCB-157	0.08	4		1.9	10
2,3,3',4,4',6-HxCB	PCB-158	0.6	4		1.9	10
2,3',4,4',5,5'-HxCB	PCB-167	0.05	4		1.1	10
2,3',4,4',5',6-HxCB	PCB-168	0.9	4		1.3	10
3,3',4,4',5,5'-HxCB	PCB-169	0.09	4		1.3	10
2,2',3,3',4,4',5-HpCB	PCB-170	0.9	4		2.1	10
2,2',3,3',4,4',6-HpCB	PCB-171	0.9	4		3.3	10
2,2',3,3',4',5,6-HpCB	PCB-177	1.3	4		3.7	10
2,2',3,3',5,5',6-HpCB	PCB-178	0.7	4		3.7	10
2,2',3,4,4',5,5'-HpCB	PCB-180	1.8	4		3.6	10
2,2',3,4,4',5',6-HpCB	PCB-183	0.9	4		3.9	10
2,2',3,4',5,5',6-HpCB	PCB-187	1.0	4		5.3	10
2,2',3,4',5,6,6'-HpCB	PCB-188	1.1	4		9.8	10
2,3,3',4,4',5,5'-HpCB	PCB-189	0.09	4		2.3	10
2,3,3',4,4',5',6-HpCB	PCB-191	0.5	4		6.3	10
2,3,3',4',5,5',6-HpCB	PCB-193	1.8	4		1.1	10
2,2',3,3',4,4',5,5'-OcCB	PCB-194	0.2	4		1.8	10
2,2',3,3',4,5,6,6'-OcCB	PCB-199	0.9	4		1.0	10
2,2',3,3',4,5,5'6'-OcCB	PCB-201	0.7	4		2.6	10
2,2',3,3',5,5',6,6'-OcCB	PCB-202	0.9	4		3.5	10
2,2',3,4,4',5,5',6-OcCB	PCB-203	0.9	4		2.2	10
2,3,3',4,4',5,5',6-OcCB	PCB-205	1.2	4		1.3	10
2,2',3,3',4,4',5,5',6-NoCB	PCB-206	0.09	4		3.8	10
2,2',3,3',4',5,5',6,6'-NoCB	PCB-208	1.1	4		1.9	10
Decachlorobiphenyl	PCB-209	0.08	4		3.4	10

* - EQL based on 10 g/ 1 L sample size and final volume of 200/50 µL

9.0 QUALITY CONTROL

This section describes the laboratory QC required for this project with the exception of conventional parameters. The laboratory QC for these parameters are described in Taylor et al. (2016). Field replicates and equipment blanks are described previously in Sections 7.2 through 7.4. Details regarding the frequency and control limits of required QC samples are provided in Tables 6 through 8. Below are general descriptions of types of laboratory QC samples.

- Analysis of method blanks is used to evaluate the levels of contamination that might be associated with the processing and analysis of samples in the laboratory and introduce bias into the sample result. Method blank results will be compared to environmental sample concentrations and validated per EPA Region 10 guidelines (EPA 1995)
- A laboratory duplicate is a second aliquot of a sample, processed concurrently and in an identical manner with the original sample. The laboratory duplicate is processed through the entire analytical procedure along with the original sample in the same quality control batch. Laboratory duplicate results are used to assess the precision of the analytical method and the relative percent difference (RPD) between the results should be within method-specified or performance-based quality control limits.
- A laboratory control sample is a sample of known analyte concentration(s) that is prepared in the lab from a separate source of analyte(s) relative to the calibration standards. Since the laboratory control sample analysis should follow the entire analytical process, it should be stored and prepared following the same procedures as a field sample. Analysis of a laboratory control sample is used as an indicator of method accuracy and long-term analytical precision.
- A spike blank is a spiked aliquot of clean reference matrix used for the method blank. The spiked aliquot is processed through the entire analytical procedure. Analysis of the spike blank is used as an indicator of method accuracy. It may be conducted in lieu of a laboratory control sample. A spike blank duplicate should be analyzed whenever there is insufficient sample volume to include a sample duplicate in the batch.
- A surrogate is a known concentration of non-target analyte which is added to each sample (both analytical and QC samples) prior to extraction and analysis for all trace organic analyses. Surrogate recovery is used as a sample-specific indication of method or matrix bias for target analytes. The surrogate is selected to behave in a similar manner to the target analytes.
- The ongoing precision and recovery (OPR) samples must show acceptable recoveries, according to the respective methods for data to be reported without qualification.

9.1 PCB Congeners

The PCB congener method provides reliable analyte identification and very low detection limits. An extensive suite of labelled surrogate standards (Table 7) is added before samples are extracted. Data are "recovery-corrected" for losses in extraction and clean-up, and analytes are quantified against their labeled analogues.

Table 7. Labeled Surrogates and Recovery Standards Used for EPA Method 1668C PCB Congener Analysis

^{13}C-labeled PCB Congener Surrogate Standards				
1	37	123	155	202
3	54	118	167	205
4	81	114	156	208
15	77	105	157	206
19	104	126	169	209
			189	
^{13}C-labeled Cleanup Standards				
28	111	178		
^{13}C-labeled Internal (Recovery) Standards				
9	52	101	138	194

QA/QC samples include method blank, OPR sample, and surrogate spikes. Method blanks and OPR, which are the same as spike blanks, are each included with each batch of samples. Surrogate spikes are labeled compounds that are included with each sample. The sample results are corrected for the recoveries associated with these surrogate spikes as part of the isotope dilution method. In addition, a laboratory duplicate will be conducted with each batch of samples. Note that a matrix spike and matrix spike duplicate are not required, nor meaningful under Method 1668C. Method 1668C has specific requirements for method blanks that must be met before sample data can be reported (see Section 9.5.2 of Method 1668C). The OPR samples must show acceptable recoveries, according to Method 1668C, to analyze the samples and report the data. A summary of the quality control samples are shown in Table 8.

Table 8. PCBs QA/QC Frequency and Acceptance Criteria

Frequency	Method Blank	Lab Duplicate (RPD)	OPR (% Recovery)	Surrogate Spikes
	1 per batch	1 per batch	1 per batch	Each sample
PCB Congeners	<LMCL[a]	RPD <50%	laboratory QC limits[b]	laboratory QC limits[b]

batch = 20 samples or less prepared as a set

[a] EPA Method 1668C blank criteria (see Table 2 of published method) is to be below the Minimum Levels: 2, 10, 50 pg/congener depending on the congener with the sum of all congeners below 300 pg/sample. Higher levels are acceptable when sample concentrations exceed 10x the blank levels.

[b] EPA Method 1668C OPR recovery criteria 60-135% for select congeners (see Table 6 of the published method) will be used as quality control limits.

9.2 Corrective Action for QC Problems

Corrective action for field measurements and laboratory analysis will follow those described in each SOP. Examples of corrective action include:

- Re-analyzing the samples
- Re-extracting the samples
- Re-preparing of the calibration verification standard for laboratory analyses
- Re-calibrating the field equipment
- Qualifying results as described in Section 10.2

9.3 Flow Data

Flow data will be checked by timing the amount of water through the peristaltic pumps per minute to confirm that the current speed setting is generating a flow of 117 mL/min per mesocosm. Results will be documented in the field sheets and the pump rotation rate adjusted as needed to maintain the proper flow rate.

9.4 Audits

Audits can help verify data quality by ensuring the QAPP is implemented correctly, and the quality of data is acceptable. To verify samples are collected according to the methods described in the QAPP, the project manager will conduct a field audit by supervising at least one sampling event for this project. Documentation will include field notes and pictures taken by the project manager. The project manager will also conduct an analytical audit by a preliminary data review; comparing analytical results, including detection limits, to the QAPP-specified goals. If review of chemistry data suggests sampling or method revisions are required, outside of those allowed in the cited methods and SOPs, an addendum to this QAPP will be prepared.

10.0 DATA MANAGEMENT, VERIFICATION, AND REPORTING

This section explains the standard practices for managing, verifying, and reporting data collected or analyzed as part of this study.

10.1 Data Storage

King County will retain records of all monitoring information, including all calibration and maintenance records and all original recordings from the flow data logger, copies of all reports generated for this study, and records of all data used in this study, for a period of at least five years.

10.2 Analytical Data Verification and Validation

10.2.1 Flow Data

Flow data will be verified by comparing metered flow rates with known volumes of water or pump run times as checks. The flow totalizer value will be used as a seasonal total. When a discrepancy is found with a pumped rate due to wear and tear on the tubing and other inefficiencies, the total volume from the totalizer (divided by time and the 12 mesocosms) will be used as the definitive value.

10.2.2 Analytical Data

Data reported by the by both WSU and Pacific Rim Laboratories, must pass a review process before final results are used. All necessary data needed for independent review of PCB congener data will be provided by Pacific Rim Laboratories. A subcontracted data validator will review the PCB congener data following EPA Level III guidelines (EPA 1995). Both data validation sets will be based on QA/QC samples and included in the final report as an appendix.

Qualifiers will be applied to analytical data during the data quality review process, and are presented in Table 10.

Table 9. Pacific Rim Laboratory Data Qualifiers

Qualifier	Description	EIM Qualifier
U	Indicates the compound was not detected at the concentration listed.	U
J	Indicates the sample concentration is less than the lowest point on the calibration curve.	J
N	Indicates the compound was not detected due to not meeting all identification criteria. The concentration is reported as the estimated maximum possible concentration (EMPC)	U, with description in Comment Field

Qualifier	Description	EIM Qualifier
B	Indicates the compound was detected in the associated method blank.	Depends on data validation (UJ, JL, or Null)
B1	Indicates the sample concentration is less than five times the concentration found in the method blank.	UJ

Additionally, equipment blank and field replicate results will be presented in the final report. If these results indicate a problem with precision or accuracy, data qualifiers may be applied based on the National Functional Guidelines (EPA 2010b and EPA 2014) and best professional judgment.

10.2.3 Rain Gauge Data

Rainfall data from the sources listed in Taylor et al. (2016) will be used to describe the magnitude and range of storm conditions during sampling events. All of these data sources provide provisional data which will only be used for project review and audit purposes. Only final data as issued by the gauge owner will be used for final analysis and reports. The primary source of rain fall data is the University of Washington's Harris Hydraulics Laboratory gauge which is approximately 800m from the study area.

10.3 Data Reduction, Review, and Reporting

Pacific Rim and WSU Laboratory personnel will be responsible for internal quality control verification, proper data transfer, and reporting data to the project manager by electronic data deliverable.

The final report of this study will include:

- A summary of TOC, DOC, TSS, and PCB concentrations in the influent and effluent.
- A summary of PCB concentrations in soils.
- A summary of storm event rainfall conditions during sampling.
- A discussion of treatment effectiveness based on data analysis.
- An appendix discussing QA/QC for the data.
- An appendix including all raw analytical data with laboratory qualifiers.
- Final data will be entered into the relational database developed by Taylor et al. 2016 by the close of the project.
- Ecology and WSU Puyallup representatives will provide a technical review of the final report.
- Final report will be available on Ecology's RSMP website http://www.ecy.wa.gov/programs/wq/stormwater/municipal/rsmp/rsmp.html.

11.0 DATA QUALITY ASSESSMENT AND DATA ANALYSIS

After data verification and validation, the project manager will conduct a data quality assessment to ensure the data satisfies the MQOs and is of sufficient quality to meet study goals. The following list outlines the steps in this process, as described in the Data Quality Assessment Guidelines (EPA 2006):

1. Review the project's objectives and sampling design.

   The first step in this process is to verify whether the execution of the sampling design satisfies the project objectives. Deviations from the QAPP and site condition anomalies will be considered as part of this step.

2. Conduct a preliminary data review.

   By reviewing the QA reports and data validation memos, the project manager can assess whether the goals of precision, bias, sensitivity, accuracy, representativeness, comparability, and completeness have been achieved, as defined in Sections 5 and 6 of this QAPP. The project manager will then explore the data by generating summary statistics and basic graphs. Any observed anomalies will be investigated. The MDL value (sample-specific) will be used as a surrogate for any non-detect results for conventional parameters. Non-detect congeners will be treated as not present (null). In general, this results in a high bias for conventional parameters, which will be addressed as appropriate in the final report. Because the PCB congener method is so sensitive relative to expected total PCB concentrations, the absence of pg/L concentrations for particular congeners is assumed to be a true condition, i.e., they are absent. Many congeners were never produced as part of commercial PCB mixtures (Aroclors) so to include all non-detect congeners using a surrogate value results in an inappropriate high bias to the data.

3. Select the statistical method.

   A rank sum test will be used for comparison between influent and effluent results, with a Wilcoxon signed-rank test for the individual mesocosms, as recommended by Ecology (2011). This will be examined on both a total PCB and individual congener basis. Since the mesocosms are expected to reduce contaminant concentrations, a one-tailed test will be used; however, if the preliminary data review suggests a possible increase in contaminant concentration, a two-tailed test will be used. Two-tailed tests may also be used to compare the new dataset to historical stormwater quality data. The project manager may decide not to include statistical analysis for congeners with low frequency of detection, due to increased uncertainty.

   Results may be pooled by storm event to increase statistical power if results are similar across the two mesocosm types (BSM alone and BSM with plants). This will be based on best professional judgment, but any conclusions will be qualified,

acknowledging these are not true replicates, despite comparable designs and identical stormwater inputs.

4. Verify the assumptions of the statistical method.

   The distribution of the datasets will determine whether parametric or non-parametric statistical tests will be implemented. The number of samples proposed for this project is not based on a power analysis, but instead on the maximum number of samples that can be collected within a reasonable budget. If variability is high within the dataset, it may result in low statistical power, meaning lower probability of detecting differences between the populations (e.g., influent vs. effluent sample results or soil concentration changes). Statistical power will be reported.

5. Draw conclusions from the data.

   In this step, statistical tests will be conducted and uncertainty of the results will also be assessed. In the final report, visual representations of the data may include scatter plots, box plots, or bar charts with error bars representing standard deviations or confidence intervals. The report will also include descriptions and detailed interpretations of the statistical results. This will include estimates of the PCB loads dosed to the mesocosms and the capacity of the mesocosms and BSM to capture those loads on both a storm by storm basis and to sequester them over multiple seasons. Suggested amendments to the sampling design for future use will also be discussed.

6. Recommendations for BMP use to treat PCBs

   The final report will discuss the utility of BSM (60/40 mix) to reduce PCB loadings from stormwater in Western Washington. Recommendations will be made based on both the removal effectiveness observed as well as the ability of BSM to sequester PCBs and prevent their release.

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Appendix: Chain of Custody Forms