Quality Assurance Project Plan
Roofing Materials Assessment: Investigation of Toxic Chemicals in Roof Runoff at the Washington Stormwater Center

Prepared by
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Washington Stormwater Center

April 2016
# Quality Assurance Project Plan

## Roofing Materials Assessment: Investigation of Toxic Chemicals in Roof Runoff at the Washington Stormwater Center

<table>
<thead>
<tr>
<th>Approved by: Signature:</th>
<th>Date: January 2013</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dr. John Stark, Principal Investigator, WSC</td>
<td></td>
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<tr>
<td>Signature:</td>
<td>Date:</td>
</tr>
<tr>
<td>Lisa Rozmyn, Project Manager, WSC</td>
<td></td>
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<tr>
<td>Signature:</td>
<td>Date:</td>
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<tr>
<td>Taylor Haskins, Researcher, WSC</td>
<td></td>
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<tr>
<td>Signature:</td>
<td>Date:</td>
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<tr>
<td>Randall Marshall, Quality Assurance Reviewer, Water Quality Program, Ecology</td>
<td></td>
</tr>
<tr>
<td>Signature:</td>
<td>Date: April 2016</td>
</tr>
<tr>
<td>Cheronne Oreiro, Project Manager, Analytical Resources, Inc. (ARI) Laboratory</td>
<td></td>
</tr>
<tr>
<td>Signature:</td>
<td>Date: April 2016</td>
</tr>
</tbody>
</table>

WSC: Washington Stormwater Center
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Abstract

The Washington State Legislature is funding the Washington Stormwater Center to continue examining the potential toxicity of runoff from roofing materials typically found in the Puget Sound basin. This study expands the 2012 to 2014 study conducted by the Washington Department of Ecology (Ecology) (Winters, et al., 2014) by assessing the aged roofing materials. As with the former study, this study design includes input from the Roofing Task Force (RTF), this study is envisioned as a pilot study that will guide future actions and evaluations.

This study will evaluate the runoff from 18 constructed 4- by 8-foot, pilot-scale roof panels which were originally located at Ecology’s headquarters facility and have been re-located to the Washington Stormwater Center in Puyallup, Washington. The roofing panels have aged four years since their installation, and releases may have changed in the aging process. This project will collect samples from up to 6 rain events from each panel and analyze them for a variety of contaminants including five metals, polycyclic aromatic hydrocarbons (PAHs), and phthalates.

The project will assess toxicity of the runoff from the roofing materials to three types of aquatic organisms. Researchers will assess the acute 48-hour toxicity of the runoff on *Ceriodaphnia dubia*, and 48-hour lethal and sublethal effects on zebra fish for six rain events. For one rain event, researchers will assess the 96-hour lethal and sublethal effects of runoff from four of the roofing panels to juvenile coho salmon.

This Quality Assurance Project Plan describes the objectives of the study and the procedures to be followed to ensure the quality and integrity of the collected data and ensure the results are representative, accurate, and complete within the scope defined by the study.
Introduction

Context of the Original Study

During the Puget Sound Toxic Chemical Assessment (2007-2011), the Washington State Department of Ecology (Ecology) applied literature values to estimate contaminant releases from various sources to the Puget Sound basin (Ecology, 2011a and b) comprising all the freshwater bodies within the 12-county watershed that ultimately flow into Puget Sound and the Strait of Juan de Fuca.

Ecology (2011a and b) estimated that approximately 88% of the zinc, 60% of the cadmium, 20% of the arsenic, and 10% of the copper released within the Puget Sound basin could be associated with roof runoff. However, regional monitoring data were lacking, and most of the literature values used by Ecology came from complete roofing systems. More data were needed to assess the relative importance of roofing as a source of metals and organic compounds to the Puget Sound basin. Thus, Ecology sought and received funding from the National Estuary Program (NEP) to conduct an assessment of roofing materials in the Puget Sound basin and determine whether roofing materials contribute to releases of toxic chemicals.

To frame and scope the investigation, Ecology conducted a thorough literature review which is documented in its initial Quality Assurance Project Plan (QAPP) (Ecology 2013). In addition the study was performed in collaboration with a Roofing Task Force (RTF) of roofing manufacturers, their associations, and other stakeholders. The RTF provided advice on the most prevalent types of roofing materials used in the Pacific Northwest. RTF members provided and installed the roofing materials on constructed panels 8 feet long and 4 feet wide. The panels studied represented 14 different types of roofing materials (with three replicates of the asphalt shingle roofing material) and two glass control panels. Roofing panels represented materials typical of commercial (low slope) and residential (steep slope) installations. Table 1 lists the types of materials assessed in the study and Figure 1 shows the installations behind the ecology headquarters building in Lacey, Washington.

Following installation of the new roofing materials Ecology collected and analyzed stormwater runoff during 20 rain events between 2013 and 2014. The study was divided into two rounds. Round 1 included 10 rain events between February and April 2013 (Round 1). To improve characterization of baseline conditions and begin to evaluate effects of weathering, Ecology also collected runoff samples during an additional 10 rain events between October 2013 and late January 2014 (Round 2). Runoff samples were analyzed for five metals (arsenic, cadmium, copper, lead, and zinc), polycyclic aromatic hydrocarbons (PAHs), and phthalates.

While the study found elevated concentrations of metals in runoff from a few of the roofing materials, runoff from the majority of the roofing materials tested was not elevated compared to the control panels. However, the investigation did identify significantly higher concentrations of one or more of the five metals in runoff from several types of roofing materials panels when compared to the glass control panels. Most notably, the following roofing panels released the highest metals concentrations: treated wood shakes released arsenic and copper, copper roofing released copper, PVC roofing released arsenic, and Zincalume® and EPDM roofing materials.
### Table 1. Roofing materials and roof panel identification codes.

<table>
<thead>
<tr>
<th>Id.</th>
<th>Roof Type</th>
<th>Description/Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Steep Slope</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AS^A</td>
<td>Asphalt shingle - composite 6 types of shingles without algal resistant (AR) copper-containing granules</td>
<td>A composite of 6 different asphalt manufacturers’ shingles commonly used in Washington without chemicals used for algae control</td>
</tr>
<tr>
<td>AAR</td>
<td>Asphalt shingle - composite 6 types of shingles with AR copper-containing granules</td>
<td>A composite of 6 different asphalt manufacturers’ shingles commonly used in Washington with chemicals used for algae control</td>
</tr>
<tr>
<td>CPR</td>
<td>Copper</td>
<td>Copper roofing panel</td>
</tr>
<tr>
<td>PAZ</td>
<td>Manufacturer-painted galvanized steel</td>
<td>Galvanized steel coated with paint applied by the manufacturer</td>
</tr>
<tr>
<td>CTI</td>
<td>Concrete tile</td>
<td>Concrete tile is generally 20-30% concrete; 50-60% sand and aggregate; 0-5% limestone and may include an acrylic coating</td>
</tr>
<tr>
<td>WOS</td>
<td>Wood shingle/shake</td>
<td>Cedar most prevalently used in Washington, with no preservative and no fire retardants</td>
</tr>
<tr>
<td>TWO</td>
<td>Manufacturer-treated wood shingle/shake</td>
<td>Treated with chromate copper arsenate (CCA) to preserve wood</td>
</tr>
<tr>
<td>GST</td>
<td>Frosted glass (control)</td>
<td>Steep slope control to subtract wet and dry air deposition</td>
</tr>
<tr>
<td><strong>Low Slope</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPO</td>
<td>Thermoplastic polyolefin (TPO)</td>
<td>A single ply thermoplastic roofing material</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinyl chloride (PVC)</td>
<td>A single ply roofing material</td>
</tr>
<tr>
<td>EPD</td>
<td>Ethylene propylene diene monomer (EPDM)</td>
<td>A rubberized single ply roofing material</td>
</tr>
<tr>
<td>BUR</td>
<td>Built-up roof (BUR) with oxidized asphalt granulated cap sheet</td>
<td>Standard commercial roofing includes asphalt felt and hot applied asphalt and an oxidized asphalt granulated cap</td>
</tr>
<tr>
<td>BUS</td>
<td>Modified BUR with styrene butadiene styrene (SBS) granulated cap sheet</td>
<td>Standard BUR with SBS added as cap</td>
</tr>
<tr>
<td>BUA</td>
<td>Modified BUR with Atatic polypropylene (APP) granulated cap sheet</td>
<td>Standard BUR with APP added as cap</td>
</tr>
<tr>
<td>ZIN</td>
<td>Zincalume®</td>
<td>An aluminum zinc alloy product that represents a high fraction of the sheet metal roofing market in Western Washington</td>
</tr>
<tr>
<td>GLO</td>
<td>Frosted glass (control)</td>
<td>Low slope control to subtract wet and dry air deposition</td>
</tr>
</tbody>
</table>
released zinc. Comparisons of concentrations in runoff from the roofing panels during Round 1 with concentrations during Round 2 identified significant reductions in metals concentrations in runoff from many of the panels within the year of panel aging.

Across the 20 rain events, the study found that asphalt shingle, built-up, modified-built-up, TPO without brominated flame retardant, concrete tile, and untreated wood shingle roofing materials did not release elevated levels of the metals evaluated in runoff.

Comparing metals concentrations in runoff from the Ecology study with concentrations used to estimate releases to the Puget Sound basin in Ecology’s 2011 study (Ecology 2011 a and b), Ecology found, with one exception, that concentrations used in the 2011 study ranged from 30% to three orders of magnitude higher. However, the 2011 study estimates primarily reflected full-scale roofing systems, rather than the single component in the 2013-2014 study: roofing materials.

The study found that concentrations of PAHs in runoff from the roofing panels were low and generally not distinguishable from concentrations from the glass control panels, even in those roofs which have asphalt components (such as asphalt shingle, built-up, and modified built-up roofing). Median total PAH concentrations in runoff from all but one panel appeared to increase in Round 2 over concentrations measured in Round 1.
Concentrations of phthalates in runoff from the roofing panels were low across all panels. Phthalates concentrations found in runoff from the treated wood shake panel (TWO) in Round 1 were no longer distinguishable from concentrations in the runoff from the glass control panel in Round 2 of the study.

Because concentrations in runoff depend on a number of factors – such as roofing materials and components, age of the materials, angle of roof installation, and climatic conditions – comparison of runoff concentrations from individual components to basin-wide releases should be undertaken cautiously. Metals concentrations in runoff were demonstrated to depend on a number of factors, such as roofing materials, age of the materials, and climatic conditions. Thus, application of runoff concentrations from roofing materials to estimate basin-wide releases should be undertaken cautiously.

During Round 1, flame retardant or polybrominated diphenyl ether (PBDE) concentrations in runoff were low and not distinguishable from concentrations from the glass control panels. During Round 2, no PBDEs were detected in runoff from any of the roofing panels.

The study recommended that runoff from the roofing panels be evaluated as the roofing materials continue to age. Specifically, Ecology recommended continued monitoring to determine the impacts of roof aging on metals release. Ecology donated the roofing panels to the Washington Stormwater Center in Puyallup, Washington for further investigations.

**Purpose of this Study**

The purpose of this investigation is to following the robust baseline data obtained during the first 20 rain events (Round 1 and 2) at Ecology with additional monitoring. After the relocation of the roofing panels to the Washington Stormwater Center (WSC) in Puyallup, Washington, the Washington State Governor’s budget included additional funding in 2015 to continue evaluation of the runoff from the roofing panels as they age. As in Rounds 1 and 2, this study will focus on obtaining information from one component of roofing systems: the roofing materials, now aged over a four-year period.

Although not often highlighted, the impact from roofing runoff into surrounding water bodies is now becoming a new area of inquiry to understand and substantiate the premise that roofing runoff is a contributor to degrading water quality that may impact aquatic life. Thus, in addition to the chemical analyses, WSC will assess the toxicity of the runoff from the roofing panels to aquatic organisms.
Project Description

This study will assess the concentrations of a number of chemicals of concern released from 4-year old roofing materials during precipitation events. The study will also assess the toxicity of the runoff from the roofing materials to three aquatic species.

WSC re-convened the Roofing Task Force (RTF) to provide input to the design of this study. The study is not intended to recommend specific products for use by the roof manufacturing community, construction contractors, roofing designers, homeowners, or others. Nor is it intended for decision-making or recommendations concerning treatment practices to reduce toxic chemicals in roof runoff. Results of this study are intended to help guide WSC, with advice from the RTF, in making recommendations for follow-up actions and investigations, as funding becomes available, to understand the role of roofing systems in releasing toxics within the Puget Sound basin.

Objectives

This study is designed to continue the focused pilot study to gain a better understanding about the range of the concentrations of selected chemicals that leach from roofing materials exposed to precipitation events that are typical in intensity and duration of those in the Puget Sound region. The primary objectives of this phase of the Roofing Assessment are to determine:

- A range of concentrations of specific metals and organic compounds chemicals released from the four-year old roofing materials by analyzing runoff from the roofing materials over six rain events over approximately a one-year period.
- Whether changes occur in chemical concentrations in the runoff between the rain events of the Ecology study and this WSC study that reflect the impacts of weathering/aging.
- Whether roofing materials release potential contaminants at different rates with different precipitation amounts, intensities, durations, or antecedent dry periods.

The specific objectives of the toxicity analysis of the study are to assess the lethal and sublethal toxicity in runoff from the 3-year old roofing materials to three aquatic organisms. The toxicity analyses will expose aquatic organisms [zebra fish embryos (*Danio rerio*), invertebrates (*Ceriodaphnia dubia*), coho salmon fry (*Oncorhynchus kisutch*)] to roof runoff to determine potential for acute toxicity. Zebra fish embryos and *C. dubia* neonates will be exposed to the runoff from all 18 roofing materials from six rain events. The coho salmon fry will be exposed to runoff from three of the roofing materials and one control in runoff from one rain event.

WSC recognizes the same limitations of the study recognized by Ecology. These include but are not necessarily limited to evaluation of:

- Roofing materials only rather than roofing systems
- Assessment of three-year old materials only
- Replicates for asphalt shingle roofs only
- A limited sample season
- A limited number of storms
**Summary of Project**

Based on the input from the RTF and consideration of an experimental design that can be most effectively implemented, the study will evaluate runoff from the 18 constructed pilot-scale roof panels including two glass controls. An additional 304-grade stainless steel panel will be constructed and included in this study to assess concentrations of conventional parameters (cations and dissolved organic carbon) as well as metals and organics in the rain water. All pilot panels are the same size and were constructed as they would be if placed on a roofing surface, to the extent possible. To assess variability, three replicate asphalt shingle panels (without algal–resistant copper-containing granules) will be sampled. Each of these samples from these replicate asphalt shingle panels will be analyzed independently. This roofing type was selected for replication since it is the most common roofing type used in the Puget Sound basin. Table 1 lists the types of roofing materials that will be evaluated.

WSC has located the pilot project roofing assemblages in a secure location at the WSC facility in Puyallup, Washington. This location ensures that all panels are exposed to the same precipitation event and the same wind direction simultaneously.

WSC will analyze runoff from roof panels from up to six rain events between April 2016 and April 2017. WSC will analyze all runoff samples for metals (arsenic, cadmium, copper, lead, and zinc) for all six rain events. WSC will analyze runoff from the roofing panels from three rain events for PAHs, and phthalates as described subsequently.

WSC will expose aquatic organisms [zebra fish embryos (*Danio rerio*) and invertebrates (*Ceriodaphnia dubia*)] to runoff from the 18 roofing panels roof runoff to determine potential for acute toxicity. Zebra fish embryos and *C. dubia* neonates will be exposed to the runoff from each of the roofing materials from six rain events. The coho salmon fry (*Oncorhynchus kisutch*) fry will be exposed to runoff from three selected roofing materials and one control in runoff from one rain event.
**Organization and Schedule**

Table 2 lists the people involved in this project. All are employees of Ecology. Table 3 presents the proposed schedule for this project.

### Table 2. Organization of project staff and responsibilities.

<table>
<thead>
<tr>
<th>Staff</th>
<th>Title</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lisa Rozmyn (253) 445-4552</td>
<td>Project Manager, WSC</td>
<td>Reviews and approves QAPP. Oversees field sampling and transportation of samples to the laboratory, with possible assistance of research assistant. Reviews the draft report and final report.</td>
</tr>
<tr>
<td>Taylor Haskins (253) 445-4552</td>
<td>Researcher, WSC</td>
<td>Conducts field research, analyzes and interprets data, and prepares draft and final report.</td>
</tr>
<tr>
<td>Nancy Winters (360) 943-3053</td>
<td>Staff, WSC</td>
<td>Prepares QAPP, assists in training Researcher on sampling procedures, reviews report</td>
</tr>
<tr>
<td>Dr. John Stark (253) 445-4505</td>
<td>Principal Investigator, WSC</td>
<td>Reviews and approves QAPP. Reviews Researcher’s work</td>
</tr>
<tr>
<td>Randall Marshall (360) 407-6445</td>
<td>Ecology Water Quality Program QA Officer</td>
<td>Reviews and approves QAPP</td>
</tr>
<tr>
<td>Cheronne Oneiro, ARI Laboratories Phone: 206-695-6200</td>
<td>Laboratory Project Manager</td>
<td>Ensures samples are analyzed in accordance with the approved QAPP</td>
</tr>
</tbody>
</table>

### Table 3. Proposed schedule for completing field and laboratory work, and reports.

<table>
<thead>
<tr>
<th>Project Element</th>
<th>Due date</th>
<th>Lead staff</th>
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<tbody>
<tr>
<td>Field work</td>
<td>April 2017</td>
<td>Taylor Haskins</td>
</tr>
<tr>
<td>Laboratory analysis</td>
<td>2 weeks following submittal of each round of samples</td>
<td>Taylor Haskins and Cheronne Oneiro, ARI</td>
</tr>
<tr>
<td>Final Report</td>
<td>June 30, 2017</td>
<td>Taylor Haskins</td>
</tr>
</tbody>
</table>

**Training**

The researcher and any other field personnel will receive training in proper operation of the equipment and sample collection and management for all standard operating procedures necessary to complete the tasks described in this QAPP. They will demonstrate to the Project Manager their ability to properly set up the runoff collection bottles, operate the tipping bucket...
rain gauge and download the data logger, mix samples, record observations in the field notebooks, and preserve, package, and track samples. Field crew will also be provided with training to safely work in wet, cold, and potentially dark conditions.

The contractor and project manager will conduct follow-up meetings with the field crew after each sampling event to trouble-shoot and to discuss methods and procedures. The project manager will also conduct a field audit after the third precipitation event to verify proper methods and techniques.

**Quality Objectives**

The primary purpose of the QAPP is to ensure data collected for the study are scientifically defensible. This section discusses the data quality objectives (DQOs) developed to ensure the study objectives are achieved in a qualitative and quantitative manner. The DQOs define the appropriate type of data and tolerable levels of potential errors. The DQOs for this study include the following:

- Data will be generated using established protocols and previously published methods for sampling, sample handling and process, laboratory analysis, and record keeping.
- Data will be representative of the chemical composition of roof runoff from known roofing materials and be of known precision, accuracy, and bias.
- Data reporting and analytical sensitivity will be clearly established and adequate for characterizing runoff from identified roofing materials.

The DQOs provide the basis of the measurement quality objectives (MQOs). MQOs provide the quantitative thresholds for data, based on data quality indicators specifically established for analytical and instrument performance. MQOs serve as performance measures described in terms of:

- Sensitivity
- Representativeness
- Precision
- Bias/Accuracy
- Comparability
- Completeness

For the two parameters that will be measured in the field (pH and specific conductance), MQOs of accuracy, bias, and sensitivity will be achieved through following standard operating procedures (SOPs) and daily calibration of the field instruments. SOPs for pH and specific conductance are EAP031 and EAP032, respectively (Ward 2006 and 2011, respectively). Daily instrument calibrations will be conducted at ambient field temperatures at the beginning of each rain sampling event using a two-point calibration. The sensitivity of the pH meter is 0.01 units using EPA method 150.2 (a hand-held meter); the meter’s precision and accuracy are ± 0.02
units. The MQO for the relative percent difference among the three replicate asphalt shingle panels is ± 20 percent. EPA method 120.1 will be used to measure specific conductance. The sensitivity of the hand-held unit ranges between 0.001 and 0.01 millisiemens per centimeter (mS/cm). The MQO for precision is 0.002 mS/cm and for accuracy is ± 5 percent of the reading or 0.001 mS/cm, whichever is greater. The MQO for the relative percent difference for specific conductance between the three replicate asphalt shingle panels is ± 20 percent.

**Sensitivity**

Sensitivity is the measure of the concentration at which an analytical method can be positively identified and analytical results reported. The sensitivity of a method is commonly called the detection limit. This term vaguely refers to either the method detection limit (MDL) or the reporting limit (RL). The QAPP specifies both MDLs and RLs (Tables 4 through 6), and requires reporting of values between these two limits with “estimation” or “J” flags for metals and a “UJ” flag for organics. The MDLs shown in Tables 4 through 6 for each analyte define the lowest concentrations of interest within budget of this project. The MQO for analytical results of equipment rinse, distilled water, and or method blanks is less than the MDL for metals and less than the RL for organics. Qualification of results based on this goal is discussed in the Data Verification/Validation section.

For the toxicity portions of the study, sensitivity will be gauged by the ability to detect a difference in lethal and sublethal effects on the species between the runoff from the roofing panels and the laboratory controls. Survival of the organisms in the laboratory controls must be at least 90% for each test. Dissolved oxygen for the juvenile coho salmon exposures must remain above 6 mg/L.

**Representativeness**

Representativeness is the extent to which a measurement actually represents true environmental conditions. One component of representativeness is selection of roofing materials to be monitored. The study provides for roofing materials and panel installations representative of typical uses in the Puget Sound basin.

Representativeness is particularly difficult to define for stormwater quality in a short-term study as it changes depending on the storm size, phase of the storm, antecedent conditions, and the surface contributing to the runoff. The representativeness of this study is also limited to the evaluation of a limited number of roofing materials, testing of roofing materials rather than roofing systems, use of new materials, sampling a single geographic location, and the short-term duration of the study.

For both the chemical and toxicological analyses, representativeness will be attained by collecting and analyzing runoff from up to six rain events with a variety of intensities and durations, from panels of known age and typical construction, and by characterizing atmospheric deposition and other contaminants that may affect the sample results. For the asphalt shingle roofs, the pilot panels will consist of a composite of the six asphalt shingle manufacturers’ products available in the Puget Sound basin, providing a broader representativeness.

This design will collect samples which represent contaminants that leach from specific types of roofing material and will ensure representativeness by collecting all runoff from each panel for
each rain event. By sampling a composite of the full rain event, the concentrations measured will represent event mean concentrations for rain events defined by this plan (i.e., rain events producing between 0.08 and 0.75 inches of rain in a day and preceded by a 6-hour period with less than 0.1 inches).

**Precision**

Precision is the degree of agreement among repeated measurements of the same parameter and gives information about the consistency of methods. It applies to all analytical techniques and field replicates. Precision is expressed in terms of the relative percent difference (RPD) between multiple measurements (e.g., A and B).

Field precision is measured by collecting blind (to the laboratory) replicate samples. The precision is then calculated using the following formula:

\[
\text{RPD} = \frac{(A-B) \times 100}{(A+B)/2}
\]

For field samples, this QAPP assesses precision in two ways. First, for the asphalt shingle roofing, three panels represent three replicates, and all three will be sampled for each rain event. Second, paired field split samples will be obtained by measuring samples obtained from the same runoff collection container to help assess precision. Field crew will obtain both a sample and a field split, one after the other, while mixing the runoff collection container, thus limiting differences in time and in settling.

The laboratory assesses its precision using the same formula by measuring the RPD between a matrix spike (MS) and matrix spike duplicate (MSD) sample. Tables 5 through 7 list acceptable RPDs for each of the parameters. Equipment rinse, distilled water, and method blanks will assist in determining reasons for poor precision.

Four replicates will be used for the zebra fish and C. dubia toxicity tests, and three replicates will be used for the coho salmon fry to maximize precision while minimizing the sacrifice of animals. Precision for each metric can be calculated as the coefficient of variation CV, the standard deviation/mean). Ideally, the CV should be less than 10% to achieve good sensitivity

**Bias/Accuracy**

Bias or accuracy is a measure of confidence that describes how close a measurement is to its “true value.” Methods to determine and assess accuracy of field and laboratory measurements include: instrument calibration, and various types of QC checks (e.g., sample split measurements, spike recoveries, continuing calibration verification checks, internal standards, field and laboratory blanks, external samples), and performance audit samples.

Accuracy will be estimated by reanalyzing a sample to which a material of known concentration has been added (a laboratory control sample [LCS] and a matrix spike [MS] sample), and the results will be expressed as percent recovery of the added pollutant.

\[
\text{Accuracy} = \frac{\text{Measured value}}{\text{True value}} \times 100
\]
Tables 4 through 6 list acceptable percent recoveries for the parameters. Water blanks (distilled water), equipment rinse blanks, and method blanks will assist in determining bias and reasons for poor accuracy. Further the glass control panels will serve as a control for bias from wet and dry deposition.

For the toxicity portions of the study, measurements will be made by the same individual to maximize accuracy. Bias will be minimized by an expert review of the measurement methods.

**Comparability**

Comparability is the degree to which data can be compared directly to similar studies. Standardized sampling techniques, standard analytical methods, and units of reporting with comparable sensitivity will be used to ensure comparability. Use of standard operating procedures for field sampling (pH and specific conductance analyses), decontamination procedures, and laboratory analyses in accordance with the *ARI’s Laboratory Quality Assurance Plan* (ARI, 2014) will also provide greater comparability. Analytical methods include U.S. Environmental Protection Agency (EPA)-approved field and laboratory methods. Staff obtaining the samples will be trained to follow standard protocols for each parameter as described in this plan. The use of pilot-scale roofing panels will generally replicate the work of Winters et al. (2014), Clark et al. (2008) and Chang et al. (2004).

For the toxicity portions of the study, methods used for this study are similar to other protocols for the same organisms published by the US. Environmental Protection Agency and the Organization for Economic Cooperation and Development (OECD). Thus, toxicity determined in this study will be comparable to toxicity assessments for the same organisms in other tests.

**Completeness**

For both the chemical and toxicological analyses, completeness is the comparison between the number of useable data points collected and the number identified in the plan. Completeness will be measured as the percentage of usable samples from the total number of planned samples from the formula:

\[
\text{Completeness} = \frac{\text{No. planned samples} - \text{No. of unacceptable/incomplete samples}}{\text{No. planned samples}} \times 100
\]

A completeness goal of 90% is established for field and laboratory parameters.

The laboratory will meet all quality control (QC) requirements of the analytical methods being used for this project. Tables 4 through 6 list the MQOs for sensitivity, precision, accuracy, and completeness.
Table 4. Measurement quality objectives for dissolved metals and conventional parameters.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Analysis/Prep Method</th>
<th>MDL(^1) (ug/L)</th>
<th>RL(^2) (ug/L)</th>
<th>Field reps &amp; Splits (RPD)</th>
<th>LCS(^3) (% R)</th>
<th>Matrix Spike (%R)</th>
<th>MS/MSD(^4) (RPD)</th>
<th>Completeness (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metals</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arsenic</td>
<td>EPA 200.8</td>
<td>0.0298</td>
<td>0.2</td>
<td>+ 20</td>
<td>80-120</td>
<td>75-125</td>
<td>+ 20</td>
<td>90</td>
</tr>
<tr>
<td>Cadmium</td>
<td>EPA 200.8</td>
<td>0.0072</td>
<td>0.1</td>
<td>+ 20</td>
<td>80-120</td>
<td>75-125</td>
<td>+ 20</td>
<td>90</td>
</tr>
<tr>
<td>Copper</td>
<td>EPA 200.8</td>
<td>0.037</td>
<td>0.5</td>
<td>+ 20</td>
<td>80-120</td>
<td>75-125</td>
<td>+ 20</td>
<td>90</td>
</tr>
<tr>
<td>Lead</td>
<td>EPA 200.8</td>
<td>0.012</td>
<td>0.01</td>
<td>+ 20</td>
<td>80-120</td>
<td>75-125</td>
<td>+ 20</td>
<td>90</td>
</tr>
<tr>
<td>Zinc</td>
<td>EPA 200.8</td>
<td>0.33</td>
<td>4.0</td>
<td>+ 20</td>
<td>80-120</td>
<td>75-125</td>
<td>+ 20</td>
<td>90</td>
</tr>
<tr>
<td><strong>Conventional Parameters</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>EPA 6010C</td>
<td>11.3</td>
<td>50</td>
<td>+ 20</td>
<td>80-120</td>
<td>75-125</td>
<td>NA</td>
<td>90</td>
</tr>
<tr>
<td>Magnesium</td>
<td>EPA 6010C</td>
<td>9.61</td>
<td>50</td>
<td>+ 20</td>
<td>80-120</td>
<td>75-125</td>
<td>NA</td>
<td>90</td>
</tr>
<tr>
<td>Sodium</td>
<td>EPA 6010C</td>
<td>11.4</td>
<td>500</td>
<td>+ 20</td>
<td>80-120</td>
<td>75-125</td>
<td>NA</td>
<td>90</td>
</tr>
<tr>
<td>DOC(^6)</td>
<td>SM5310B</td>
<td>500</td>
<td>500</td>
<td>+ 20</td>
<td>80-120</td>
<td>75-125</td>
<td>NA</td>
<td>90</td>
</tr>
</tbody>
</table>

1 MDL: Method detection limit
2 RL: Reporting limit
3 LCS (%R): Laboratory control sample (percent recovery)
4 MS/MSD: Matrix spike/matrix spike duplicate
5 NA Not applicable
6 Dissolved Organic Carbon
Table 5. Measurement quality objectives for PAHs.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Analysis/ Prep. Methods</th>
<th>Method Detect. Limit (ug/L)(^1)</th>
<th>Report Limit(^2) (ug/L)</th>
<th>Field Reps. &amp; Splits (RPD)</th>
<th>LCS(^3) (%R)</th>
<th>Matrix Spike (%R)</th>
<th>MS/ MSD (RPD)</th>
<th>Complete -ness (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Methylnaphthalene</td>
<td>SW 8270DSIM/ SW 3535A</td>
<td>0.00313</td>
<td>0.01</td>
<td>±40</td>
<td>29-120</td>
<td>29-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>2-Methylnaphthalene</td>
<td>SW 8270DSIM/ SW 3510C</td>
<td>0.00384</td>
<td>0.01</td>
<td>±40</td>
<td>37-120</td>
<td>37-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>SW 8270DSIM/ SW 3510C</td>
<td>0.00311</td>
<td>0.01</td>
<td>±40</td>
<td>41-120</td>
<td>41-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>SW 8270DSIM/ SW 3510C</td>
<td>0.00317</td>
<td>0.01</td>
<td>±40</td>
<td>41-120</td>
<td>41-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Anthracene</td>
<td>SW 8270DSIM/ SW 3510C</td>
<td>0.00248</td>
<td>0.01</td>
<td>±40</td>
<td>40-120</td>
<td>40-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Benzo(a)anthracene</td>
<td>SW 8270DSIM/ SW 3510C</td>
<td>0.00347</td>
<td>0.01</td>
<td>±40</td>
<td>42-120</td>
<td>42-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Benzo(a)-pyrene</td>
<td>SW 8270DSIM/ SW 3510C</td>
<td>0.00237</td>
<td>0.01</td>
<td>±40</td>
<td>35-120</td>
<td>35-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Benzo(b)fluoranthene</td>
<td>SW 8270DSIM/ SW 3510C</td>
<td>0.00356</td>
<td>0.01</td>
<td>±40</td>
<td>44-123</td>
<td>44-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Benzo-(g,h,i)-perylene</td>
<td>SW 8270DSIM/ SW 3510C</td>
<td>0.00312</td>
<td>0.01</td>
<td>±40</td>
<td>38-120</td>
<td>38-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
<td>SW 8270DSIM/ SW 3510C</td>
<td>0.00345</td>
<td>0.01</td>
<td>±40</td>
<td>50-120</td>
<td>50-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Chrysene</td>
<td>SW 8270DSIM/ SW 3510C</td>
<td>0.00313</td>
<td>0.01</td>
<td>±40</td>
<td>44-120</td>
<td>44-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Dibeno(a,h)anthracene</td>
<td>SW 8270DSIM/ SW 3510C</td>
<td>0.00303</td>
<td>0.01</td>
<td>±40</td>
<td>34-120</td>
<td>34-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Dibenzofuran</td>
<td>SW 8270DSIM/ SW 3510C</td>
<td>0.00354</td>
<td>0.01</td>
<td>±40</td>
<td>38-120</td>
<td>38-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>SW 8270DSIM/ SW 3535A</td>
<td>0.00338</td>
<td>0.01</td>
<td>±40</td>
<td>45-120</td>
<td>45-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Fluorene</td>
<td>SW 8270DSIM/ SW 3510C</td>
<td>0.00317</td>
<td>0.01</td>
<td>±40</td>
<td>44-120</td>
<td>44-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Indeno(1,2,3cd)pyrene</td>
<td>SW 8270DSIM/ SW 3510C</td>
<td>0.00334</td>
<td>0.01</td>
<td>±40</td>
<td>37-120</td>
<td>37-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>SW 8270DSIM/ SW 3510C</td>
<td>0.00740</td>
<td>0.01</td>
<td>±40</td>
<td>37-120</td>
<td>37-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>SW 8270DSIM/ SW 3510C</td>
<td>0.00299</td>
<td>0.01</td>
<td>±40</td>
<td>41-120</td>
<td>41-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Pyrene</td>
<td>SW 8270DSIM/ SW 3510C</td>
<td>0.00417</td>
<td>0.01</td>
<td>±40</td>
<td>41-120</td>
<td>41-120</td>
<td>±30</td>
<td>90%</td>
</tr>
</tbody>
</table>

\(^1\) MDL: Method detection limit  
\(^2\) RL: Reporting limit  
\(^3\) LCS (%R): Laboratory control sample (percent recovery)  
\(^4\) MS/MSD: Matrix spike/matrix spike duplicate
Table 6. Measurement quality objectives for phthalates.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Analysis / Prep. Methods</th>
<th>MDL(^1) (ug/L)</th>
<th>RL(^2) (ug/L)</th>
<th>Field Reps/ Splits (RPD)</th>
<th>LCS(^3) (%R)</th>
<th>Matrix Spike (%R)</th>
<th>MS/ MSD(^4) RPD</th>
<th>Completeness (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis (2-Ethylhexyl) phthalate</td>
<td>SW 8270D/ SW 3510C</td>
<td>0.093</td>
<td>0.2</td>
<td>±40</td>
<td>34-130</td>
<td>34-130</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Butylbenzylphthalate</td>
<td>SW 8270D/ SW 3510C</td>
<td>0.026</td>
<td>0.2</td>
<td>±40</td>
<td>45-132</td>
<td>45-132</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Diethylphthalate</td>
<td>SW 8270D/ SW 3510C</td>
<td>0.051</td>
<td>0.2</td>
<td>±40</td>
<td>50-120</td>
<td>50-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Dimethylphthalate</td>
<td>SW 8270D/ SW 3510C</td>
<td>0.027</td>
<td>0.2</td>
<td>±40</td>
<td>43-120</td>
<td>43-120</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Di-n-Butylphthalate</td>
<td>SW 8270D/ SW 3510C</td>
<td>0.034</td>
<td>0.2</td>
<td>±40</td>
<td>48-126</td>
<td>73-148</td>
<td>±30</td>
<td>90%</td>
</tr>
<tr>
<td>Di-N-Octylphthalate</td>
<td>SW 8270D/ SW 3510C</td>
<td>0.040</td>
<td>0.2</td>
<td>±40</td>
<td>28-124</td>
<td>28-124</td>
<td>±30</td>
<td>90%</td>
</tr>
</tbody>
</table>

\(^1\) MDL: Method detection limit  
\(^2\) RL: Reporting limit  
\(^3\) LCS (%R): Laboratory control sample (percent recovery)  
\(^4\) MS/MSD: Matrix spike/matrix spike duplicate
Study Design

Roofing Types and Products

Originally, Ecology staff selected the types of roofing materials to evaluate with input from the RTF. The roofing types selected for testing are listed in Table 1. Roofing material types were selected based on three criteria:

1. Proportion of roofing types that comprise more than one percent of the surface area in the Puget Sound basin, as described in Appendix B of Ecology (2011a) and summarized in Table 7 below
2. New and emerging roofing technologies that the RTF added to the list to capture a greater spectrum of materials
3. Materials the manufacturers recommended.

Table 7. Percentage of roofing surface area in the Puget Sound basin represented by each roof type.

<table>
<thead>
<tr>
<th>Roof Type</th>
<th>Percent of Puget Sound Basin Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asphalt Shingle</td>
<td>71%</td>
</tr>
<tr>
<td>Built-up</td>
<td>13</td>
</tr>
<tr>
<td>Wood Shingle</td>
<td>6.5</td>
</tr>
<tr>
<td>Metal</td>
<td>5.3</td>
</tr>
<tr>
<td>Concrete tile</td>
<td>2.9</td>
</tr>
<tr>
<td>Copper</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Clay Tile</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Masonite</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Other</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>


Pilot-Scale Roofing Panels

Ecology staff and manufacturers’ representatives constructed 18 roofing pilot panel assemblages. The 18 panels included 14 different roofing material types, triplicate panels of the asphalt shingle without algae-resistant, copper-containing granules roofing material, and two glass controls. Gromaire et al. (2010) concluded that even small test panels provide appropriate approximations for determining stormwater runoff concentrations from roofing materials. In the original study, the glass controls were used and will continue to be used to subtract out the pollutant contribution from wet and dry deposition. Ecology constructed panel assemblages to hold each steep slope roof type at a 26.5° angle from the horizontal. This angle was selected because it is a frequently installed residential roof slope (i.e., between 4:12 and 6:12 slope) (Malarkey, pers. comm., 2012). The low slope roof types and one control were sloped at an industry-standard of 1.2° (1/4:12 slope) (ARMA, 2012). Figure 1 depicts the pilot-scale panels used in this study.
Ecology staff constructed a frame for each 4 ft. by 8 ft. panel. The panels, except for glass (controls), were provided by the manufacturers. The manufacturers or their representatives installed the panels at the Ecology investigation site, as they would be constructed on an actual roof, to the extent feasible. Manufacturers/associations were encouraged to install their roofing panels with nails, fasteners, adhesives or other seaming materials in proportion to those found on a constructed roof. Panels did not include flashing materials, gutters and downspouts, or any HVAC systems.

In 2014 when the panels were re-located to the WSC site in Puyallup, Washington, the original slopes were maintained. All panels face south-southwest at 208° of magnetic north, the approximate direction of the panels in the previous study based on the prevailing wind direction in Lacey, Washington (OWSC, 2012). Panel assemblages will be re-leveled prior to the commencement of this portion of the investigation. The panels were placed in two rows with the Ecology with the triplicate asphalt shingle panels at the end of the steep slope row. In the new location at WSC, panels are located at least 100 feet from trees or other potential obstructions to precipitation. They are a minimum of 3 feet from the ground surface at the lower edges and on 10-foot centers from one another to prevent splash from the ground or adjacent panels. Because of the rural location, a security fence was deemed unnecessary. This new location will ensure that all panels are exposed to the same precipitation event and the same wind direction simultaneously.

Based on input from the Roofing Task Force in March of 2016, a 304-grade stainless steel panel will be constructed and collocated with the original panels. The panel will be deployed immediately prior to the first rain event. The purpose of this panel is to collect runoff for chemical analysis which reflects wet deposition and rain water quality. Runoff will be collected from the panel to measure the concentrations of conventional parameters [calcium, magnesium, sodium and dissolved organic carbon (DOC)] in the rain water, as well as metals, and organic compounds. Subtraction of concentrations in runoff from the stainless steel panels from those from the glass controls panels will allow quantification of the wet and dry aerial deposition on smooth surfaced panels.

Runoff from the pilot panels will flow into Teflon®-lined high density polyethylene (HDPE) gutters to prevent potential contamination from the HDPE leaching constituents into the runoff. The gutters will be put in place prior to the commencement of the investigation and left in place between rain events.

Each gutter will drain into a 56-liter (15-gallon) stainless-steel runoff collection container. The stainless-steel collection container (set in an ice bath to preserve the samples) will be placed under cover to prevent rain from entering the container.
WSC staff will collect samples from rain events generating at least 5.2 liters (minimum required for metals and toxicological analyses) but not more than 56 liters (container maximum). The samples represent a rainfall event and will provide the equivalent of an event mean concentration. WSC will deploy a tipping bucket rain gauge and data logger at the site to monitor rain intensity and depth. The volume collected from each roofing panel will be measured at the end of a rain event.

**Monitoring and Predicting Rain Events**

WSC will install a tipping bucket rain gauge onsite at the WSC facility in Puyallup, Washington to monitor rain depth and intensity. The rain gauge tips and records at least every 0.01 inch of precipitation. The rain gauge will be operated for the entire length of the study. Downloads from the equipment will be available in real time to allow field staff to monitor the volume of rain events for sampling decision-making.

Satellite imagery and model predictions will serve as the basis for determining whether a rain event will be sampled. Weather information from one or more of the following sources will be evaluated for the Puyallup area on at least a daily basis from:

- National Weather Service Forecast Office operated by the National Oceanic and Atmospheric Administration (NOAA) [www.wrh.noaa.gov/sew](http://www.wrh.noaa.gov/sew)
- KOMO news at [www.komonews.com/weather](http://www.komonews.com/weather)

If a rain event appears imminent, field crew will prepare to sample by deploying collection equipment and notifying the laboratory.
Rain Event Definition and Number

For adequate samples to be gathered for analysis, a rain event must generate 7.5 liters of runoff when both metals and organics will be analyzed. Assuming that all precipitation hitting a 4 x 8 foot panel of roofing material runs off, the minimum rainfall required to generate 7.5 liters is 0.1 inch or 2.54 mm. However, when only metals analyses will be conducted, a smaller rain event may be sampled. The maximum rain event to be monitored can generate no more than 56 liters (15 gallons) of runoff, based on the size of the stainless-steel collection container. This maximum volume represents a 0.75-inch rain event. Sampling of rain events will not exceed 24 hours and may be interrupted to prevent container overflow.

The goal is to have a minimum antecedent dry period between rain events of 6 hours of less than 0.1 inch of precipitation. This definition differs from that described by the Ecology TAPE protocols (Ecology, 2011c) but mirrors that in the Stormwater General Permits for Municipal Separate Storm Sewer Systems. The definition of a rain event will allow WSC to capture the appropriate runoff volumes for analysis, while allowing for low intensity or long duration events.

WSC will collect and analyze runoff samples from a maximum of 6 rain events less than 0.75 inches between April 2016 and April 2017. WSC will make every attempt to sample a first flush event. The first flush rain event for this study will be defined as the first precipitation after a period of 30 days with no measurable precipitation. This is likely to occur in the late summer or autumn of 2016.

Analyses

Runoff samples from all roof types will be analyzed for five dissolved metals (arsenic, cadmium, copper, lead, and zinc). These metals were reported in the Puget Sound Toxics Assessment to contribute a measurable proportion to the metals released within the Puget Sound basin (Ecology 2011a). Measurement of dissolved metals rather than total metals was recommended by the Roofing Task Force as the dissolved portion of the metals are generally more toxic to aquatic organisms.

Runoff from all panels and from three rain events (including the first fall flush event and a late winter event) will also be analyzed for PAHs, and phthalates. Evidence of PAHs and phthalates in runoff from roofing materials has been documented in the literature (Appendix A of Ecology 2013), although it is uncertain whether all of these chemicals originate in the roofing materials or from atmospheric deposition. The Draft PAH Chemical Action Plan (Ecology 2012b) identified roofing as a potential source of PAHs that needed to be evaluated. Table 8 lists chemical parameters that will be analyzed by roofing type.

Staff will also collect samples of the runoff from the newly constructed stainless steel panel for analyses of calcium, magnesium, sodium, and DOC as described in Table 4 as well as metals, PAHs, and phthalates.
Table 8. Analyses by roofing type for the six rain events.

<table>
<thead>
<tr>
<th>Roof Type</th>
<th>Dissolved Metals</th>
<th>PAHs, Phthalates</th>
<th>Conventional</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Steep Slope</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Asphalt shingle - composite 6 types of shingles without copper-containing granules for algae control</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Asphalt shingle - composite 6 types of shingles with copper-containing granules for algae control</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Copper</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Manufacturer-painted galvanized steel</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Concrete tile</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Wood shingle/shake</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Manufacturer-treated wood shingle/shake</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td><strong>Low Slope</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermoplastic polyolefin (TPO)</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Polyvinyl chloride (PVC)</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Ethylene propylene diene monomer (EPDM)</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Zincalume®</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Built-up roof (BUR) with oxidized asphalt granulated cap sheet</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Modified BUR with SBS granulated cap sheet</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Modified BUR with APP granulated cap sheet</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td><strong>Controls</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steep slope glass control</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Low slope glass control</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Stainless steel control</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>
Sampling Procedures

Field staff will deploy a tipping bucket rain gauge and data logger at the WSC facility in Puyallup, Washington. The rain gauge tips and records every 0.01 inches of precipitation. Prior to a predicted rain event, field staff will ensure that all equipment is in working order and will call the laboratory staff to confirm the timing and anticipated number of samples. Because the shortest holding time following preservation for a sample is seven days, samples of rain events may be obtained seven days a week.

Runoff samples collected in 56-liter (15-gallon) containers represent a composite of the runoff from a panel for the rain event. Stainless-steel runoff containers will be decontaminated initially and between rain events. Runoff collection containers and Teflon® tubing will be dedicated to each roof panel type. Decontamination procedures for all materials are described in Appendix A. Equipment rinse samples will be obtained to ensure all equipment is contaminant-free (see Appendix A).

During a rain event, field staff will determine whether gutters need to be removed to prevent runoff from over topping the stainless-steel containers. At each sample location, staff will measure and record the volume of each stainless-steel runoff container and download data from the rain gauge data logger. Field staff will mix the runoff in the stainless-steel runoff container with a stainless-steel mixing device, while transferring a sample to the appropriate laboratory pre-cleaned sample bottles with a peristaltic pump and Teflon® tubing as described in Appendix A. Field splits MS, and MSD samples of runoff will be taken from three of the roofing panels. These will be selected randomly and will be sampled immediately after obtaining the original sample and while continuing to mix the contents of the stainless-steel runoff container.

Staff will also measure and record the pH and specific conductance of the runoff collected in each stainless-steel container as described in Appendix A and following Ecology’s standard operating procedures EAP031 and EAP032 (Ward 2006 and 2011, respectively).

The laboratory staff will add preservatives as needed. Table 9 describes the appropriate sample containers, required sample volumes, sample containers, preservation methods, and holding times.

Field staff will apply the prepared labels to each sample bottle. For the chemical analyses, staff will package samples in bubble wrap (or otherwise ensure the bottles will not break), complete a chain of custody form for each cooler, add ice to the coolers and seal them. Coolers will be transported to the laboratory within 2 days of collection as described in Appendix A. An example chain of custody form specific to this project is provided in Appendix A. For the toxicological analyses, sample bottles will be labeled and used in toxicity tests.

An equipment rinse blank (for each of the analytical methods) will be collected as a composite of all decontaminated equipment (stainless-steel collection container, mixing devices, tubing, and measuring device) for each rain event as described in Appendix A. Distilled deionized water from the laboratory will be used of all the post-decontamination equipment rinse samples. A
sample of the laboratory distilled and deionized water will also be analyzed for all parameters for each rain event.

Field staff will record all sampling and field information in the field logbook for each event as described in Appendix A, and will download data from the rain gauge data logger.

**Table 9. Sample bottles, preservation, and holding times.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>Sample Matrix</th>
<th>Sample Size</th>
<th>Bottles</th>
<th>Field/Lab Preservation</th>
<th>Holding time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved metals (As, Cd, Cu, Pb, Zn)</td>
<td>EPA 200.8</td>
<td>water</td>
<td>500 mL</td>
<td>500 mL HDPE</td>
<td>Cool to &lt;6°C/ Lab: filter &amp; HNO₃ to pH&lt;2</td>
<td>6 months</td>
</tr>
<tr>
<td>PAHs</td>
<td>EPA 8270D SIM</td>
<td>water</td>
<td>1 L</td>
<td>1 L amber glass</td>
<td>Cool to &lt;6°C/ H₂SO₄ to pH&lt;2 in lab</td>
<td>7 days to extraction/ 14 days after extraction</td>
</tr>
<tr>
<td>Phthalates</td>
<td>EPA 8270D</td>
<td>water</td>
<td>1L</td>
<td>1 L amber glass</td>
<td>Cool to &lt;6°C/ H₂SO₄ to pH&lt;2 in lab</td>
<td>7 days to extraction/ 14 days after extraction</td>
</tr>
<tr>
<td>Cations (Ca, Mg, Na)</td>
<td>EPA 6010C</td>
<td>water</td>
<td>500 mL</td>
<td>500 mL HDPE</td>
<td>Cool to &lt;6°C/ Lab filter &amp; HNO₃ to pH&lt;2</td>
<td>6 months</td>
</tr>
<tr>
<td>DOC</td>
<td>SM5310B</td>
<td>water</td>
<td>250 mL</td>
<td>250 mL amber glass</td>
<td>Cool to 6°C/ Lab filter &amp; H₂SO₄ to pH &lt;2</td>
<td>48hr to filtration/28 days after filtration</td>
</tr>
<tr>
<td>C. dubia acute toxicity</td>
<td>U.S. EPA, 2002a &amp; b</td>
<td>water</td>
<td>150 ml</td>
<td>250 ml amber glass</td>
<td>Use in tox test within 36 hrs</td>
<td>36 hours</td>
</tr>
<tr>
<td>Zebra fish acute toxicity</td>
<td>McIntyre et al. 2014</td>
<td>water</td>
<td>150 ml</td>
<td>250 ml amber glass</td>
<td>Use in tox test within 36 hrs</td>
<td>36 hours</td>
</tr>
<tr>
<td>Coho salmon lethal &amp; sublethal toxicity</td>
<td>U.S. EPA, 2002a &amp; b</td>
<td>water</td>
<td>30 L</td>
<td>amber glass</td>
<td>Use in tox test within 36 hrs</td>
<td>36 hours</td>
</tr>
</tbody>
</table>
Measurement Procedures

Table 10 lists the chemical analyses to be performed and the number of samples anticipated for each rain event. Estimated costs for analyses are provided in Appendix B. The WSU staff will notify the laboratories when precipitation of ample volume is anticipated and will confirm just before samples are processed to notify the laboratory of anticipated schedule of delivery. The sampling schedule will depend on specific rainfall events. Table 11 describes the range of anticipated metals concentrations based on the results of the previous Ecology study (Winters et al., 2014).

Tables 4, 5, and 6 list the reporting limits, and method detection limits. Laboratory staff will report values for all analytes at or above the method detection limit (MDL). Values between the MDL and the reporting limit (RL) will be qualified as estimated (“J” flagged).

Table 10. Numbers of samples for analysis for full suite sampling events.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dissolved Metals</th>
<th>PAHs &amp; Phthalates</th>
<th>Conventional Parameters</th>
<th>C. dubia</th>
<th>Zebra fish</th>
<th>Coho salmon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Panels</td>
<td>19</td>
<td>19</td>
<td>1</td>
<td>18</td>
<td>18</td>
<td>4</td>
</tr>
<tr>
<td>QA and Other Samples</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Field splits/replicates</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>4</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>MS+MSD</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Distilled deionized water blank</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Equipment rinse blank</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total Samples/Event</td>
<td>28</td>
<td>28</td>
<td>3</td>
<td>72</td>
<td>72</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 11. Range of concentrations (in ug/L) anticipated based on Winters, et al. (2014).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low Concentration (ug/L)</th>
<th>High Concentration (ug/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arsenic</td>
<td>&lt;0.02</td>
<td>932</td>
</tr>
<tr>
<td>Cadmium</td>
<td>&lt;0.01</td>
<td>0.09</td>
</tr>
<tr>
<td>Copper</td>
<td>&lt;0.01</td>
<td>1,985</td>
</tr>
<tr>
<td>Lead</td>
<td>0.002</td>
<td>2.36</td>
</tr>
<tr>
<td>Zinc</td>
<td>&lt;0.1</td>
<td>108</td>
</tr>
<tr>
<td>Organics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sum of detected PAHs</td>
<td>0.01</td>
<td>0.32</td>
</tr>
<tr>
<td>Sum of detected phthalates</td>
<td>&lt;0.005</td>
<td>4.2</td>
</tr>
</tbody>
</table>
Toxicological Analyses

To test the toxicity of runoff from the roofing materials from 6 rain events, WSC will primarily use models for fish (zebrafish; *Danio rerio*) and aquatic invertebrates (*Ceriodaphnia dubia*). Zebrafish and *C. dubia* are useful models for assessing the toxicity of urban runoff (McIntyre et al. 2014, 2015, 2016). Effects range from mortality to cardiovascular toxicity (*D. rerio*) and reproductive impairment (*C. dubia*).

Runoff from one rain event and a limited number of the roofing materials will also be tested on juvenile coho salmon. In addition to being a native species of concern in the Puget Sound region, juvenile coho are particularly sensitive to contaminants in urban runoff (McIntyre et al. 2015, 2016). Because of the limited number of fish available, WSU will perform this test in triplicate on runoff from three types of roofing materials and one glass control.

*Ceriodaphnia dubia*

Toxicity tests with the invertebrate *C. dubia* will follow previously published methods (U.S. EPA 2002a and b as cited in McIntyre et al. 2015). Ten neonates (<24 hours old) each will be exposed to the thawed samples of runoff from each of the roofing materials. Four replicates will be used to assess the impact of runoff from each roofing material on survival at 48 hours. The *C. dubia* toxicity test will be conducted on runoff from all six rain events.

WSU staff will perform two types of controls (field and laboratory) for each toxicity screen; the field control will be runoff from the low-slope glass roof. This control was selected because rain has a longer exposure to potential contaminants leached from the glass. The laboratory control will use daphnia rearing water. All glassware will be decontaminated following the protocols described in Appendix A.

*Zebrafish*

Methods will follow previously published methods for urban runoff toxicity to zebrafish embryos (McIntyre et al. 2014). The WSU researcher will expose embryos to thawed runoff samples for 48 hours beginning at 2 to 4 hours post-fertilization (hpf). Four replicates of 15 embryos will be used to assess the impact of runoff on survival, hatch timing, and morphometric endpoints. Runoff samples will be thawed the day before testing begins.

Embryos will be imaged at test termination and morphometrics measured (physical attributes) from digital images or videos. WSU will perform two types of controls (field and laboratory) for each toxicity screen; the field control will be runoff from the low-slope glass roof. This control was selected because rain has a longer exposure to potential contaminants leached from the glass. The laboratory control will use fish rearing water.

Glassware will be decontaminated following the protocols described in Appendix A.

*Juvenile Salmon*

For a subset of roofs that indicate possible sublethal toxicity to zebrafish embryos, runoff will be tested on juvenile coho salmon. These tests will follow protocols described in U.S. EPA (2002a and b) as cited in McIntyre et al. 2015 and 2016. The WSU researcher will conduct triplicate analyses of 10 juvenile coho salmon on thawed runoff samples from three roofing material types,
plus the field control (runoff from the low slope glass panel), and a laboratory control (fish rearing water). For the coho salmon toxicity analyses, a 50% or greater dilution may be necessary depending on the volume available from the rain event sampled.

Before the salmon trial begins, results of the chemical toxicological analysis from at least one of the rain events will need to be completed. These data will be used to select two of the roofing types that will be utilized for the test. The third roofing material will be the copper roof, due to dissolved copper’s high acute toxicity to aquatic organisms at low concentrations; Runoff from the low slope glass panel will serve as the control.

Prior to toxicity testing, aquaria will be decontaminated following McIntyre et al. (2014) as described in Appendix A. Fish will be exposed to runoff in glass aquaria set in a water bath to maintain the temperature at 13°C. Each aquarium will contain 30 L of runoff or laboratory water and receive supplemental aeration. Exposure will extend for 96 hours with daily monitoring of water quality conditions (temperature, pH, dissolved oxygen, conductivity). Fish survival and behavior will also be monitored daily.

### Quality Control Procedures

#### Field Quality Control

Two parameters will be analyzed in the field for the pilot-scale roof study, pH and specific conductance, following Ecology’s SOPs EAP031 and EAP032, respectively (Ward 2006 and 2011). Because rain water has low ionic strength, WSC staff will try to purchase a low ionic strength probe to measure pH. This will prevent drift of the pH meter associated with low ionic strength solutions. The instruments will be calibrated in the field at the beginning of each sample event in accordance with the manufacturer’s instructions. If pH or specific conductance measurements are outside of the anticipated ranges, the instrument will be re-calibrated.

Prior to the first rain event, the field staff and project manager will conduct a practice sampling run with this QAPP in hand. This will ensure that any issues are identified and resolved prior to the first rain event that will be sampled.

Field crew will collect samples with proper technique as described in the Sampling Procedures section and Appendix A of this project plan. Field replicates samples for the asphalt shingle panels (without AR) will be collected for all three panels for each rain event. Three field splits will be collected for analytical metals and organics analyses for each rain event sampled. One field split will be collected for the conventional parameters from the stainless steel panel. Runoff water for MS/MSDs will be collected as shown in Table 10 at a rate of 10% of the roof runoff samples or one per rain event, whichever is greater. Field staff will randomly select specific roofing materials for field split samples and MS/MSDs, as adequate volume is available. Precision goals for field replicates and field splits are listed in Tables 4 through 6. Field staff will collect each sample from the stainless-steel runoff container, using a peristaltic pump during continuous mixing (mixing procedures are described in Appendix A).

For the toxicological tests of *C. dubia* and zebra fish, field staff will collect eight 150 ml subsamples from the runoff from each roofing panel for replicate analyses. These subsamples
will be used within 36 hours of collection for toxicity testing with zebrafish and *C. dubia*. Similarly, field staff will collect sufficient runoff (90 L) from four roofing materials for the coho salmon toxicological analyses. These samples will also be stored at -20° C for subsequent toxicity testing.

Prior to the first rain event, field staff will collect final distilled water rinses from at least three of the cleaned gutters to ensure proper cleaning. A composite of these equipment rinse samples will be analyzed for all parameters of concern.

Field staff will collect one equipment rinse blank per rain event by pouring laboratory-provided distilled water over the cleaned equipment (runoff collection containers, tubing, stirring device, and measuring device). For each rain event, field staff will request that distilled water blanks be analyzed to determine whether the distilled water contains any of the contaminants of concern.

**Laboratory Quality Control**

The laboratory quality control procedures routinely followed by the lab will satisfy the purposes of this project. ARI will follow standard operating procedures as described in the *ARI Laboratory Quality Assurance Plan* (ARI, 2014). ARI is a Washington State accredited laboratory under chapter 173-50 of the Washington Administrative Code for the analytical methods that will be analyzed in this project. Table 12 lists the laboratory quality control samples that will be used for this project.

The field splits will replace laboratory duplicates for assessing overall precision. They will be taken from the same 56-liter (15-gallon) runoff container while mixing. These will be analyzed at a rate of 10% of the roof runoff samples or once per rain event, whichever is greater. The field crew will also collect and the laboratory will analyze MS/MSD samples for metals, PAHs, and phthalates. The field split samples will be blind to the laboratory. The laboratory will take corrective action if QC samples do not meet the measurement quality objectives in Tables 4 through 6.
Table 12. Laboratory quality control samples for pilot-scale roof runoff study.

<table>
<thead>
<tr>
<th>Parameter (Method)</th>
<th>LCS&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Method Blank</th>
<th>Field Split / Analytical Duplicate</th>
<th>MS/MSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved metals (As, Cd, Cu, Zn)</td>
<td>1/batch&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1/batch</td>
<td>3/rain event</td>
<td>10% of samples or 1/rain event whichever is greater</td>
</tr>
<tr>
<td>PAHs</td>
<td>1/batch</td>
<td>1/batch</td>
<td>3/rain event</td>
<td>10% of samples or 1/rain event whichever is greater</td>
</tr>
<tr>
<td>Phthalates</td>
<td>1/batch</td>
<td>1/batch</td>
<td>3/rain event</td>
<td>10% of samples or 1/rain event whichever is greater</td>
</tr>
<tr>
<td>Cations (Ca, Mg, Na)</td>
<td>1/batch</td>
<td>1/batch</td>
<td>1/rain event</td>
<td>NA</td>
</tr>
<tr>
<td>DOC</td>
<td>1/batch</td>
<td>1/batch</td>
<td>1/rain event</td>
<td>1/batch</td>
</tr>
</tbody>
</table>

<sup>a</sup> LCS: Laboratory control sample
<sup>b</sup> One batch consists of 20 samples or less
Data Management Procedures

Field notebook pages for each event and completed chain of custody forms will be scanned and maintained in pdf format on WSC’s computer storage drive. The project manager or designee will tabulate data and information from the chain of custody form and the field notebook (Appendix A). ARI will provide analytical results in electronic data deliverable (EXCEL spreadsheet) format. The project manager will compile analytical results and field information in tabular form for comparisons between the types of roofing material in the report. All tabular data will be stored on WSC’s computer storage drive until it is incorporated into the report.

Data Verification and Validation

The WSC researcher will examine data for errors or omissions and compliance with QC acceptance criteria. The WSC researcher will check field notebooks for missing or improbable measurements at the end of a sampling event. The WSC researcher will review field notes, correct missing data, and highlight unusual data for subsequent project manager consideration. The WSC researcher will enter corrected data into an Excel spreadsheet. The project manager will review the spreadsheet data to ensure that potential outlier data have been resolved and will review 20% of the entries for accuracy.

Laboratory results will be verified and qualified by qualified, experienced laboratory staff following the procedures outlined in the ARI Data Reporting Qualifiers (ARI, 2013). Laboratory personnel will check results for missing and improbable data. Variability in field/laboratory duplicates also will be quantified using the procedures outlined in the Laboratory QA Plan (ARI, 2014). ARI personnel will identify and qualify any estimated results (values between the MDL and the RL); the use of these values may be restricted as appropriate. Data may be qualified for other reasons including:

- Exceedance of a holding time.
- Results for organic parameters that are less than the RL (U qualified).
- Results that are between the MDL and the RL (J qualified for metals and UJ qualified for organics).
- MS/MSD results that do not meet the precision and accuracy goals in Tables 4 through 6.
- Laboratory control samples and method blanks that do not meet the precision and accuracy goals in Tables 4 through 6.

ARI will send a standard case narrative of laboratory quality assurance/quality control results for each set of samples to the project manager.

The researcher will check data received from ARI for omissions, will review the data for reasonableness and consistency, and will confirm that the data meet the measurement quality objectives of the project. The researcher will add qualifiers to the electronic data deliverable for the following reasons:

- Exceedance of the pre-preservation holding time for dissolved metals.
• Runoff results for a parameter that is less than five times the distilled water blank for that parameter.
• Runoff results for a parameter that is less than five times the equipment rinse blank for that parameter.

The researcher will qualify results that do not meet quality assurance requirements using appropriate qualifiers and will provide an explanation in a quality assurance memorandum attached to the data package.

Data validation involves a detailed examination of the data package using professional judgment to determine whether MQOs for instrument calibration, precision, bias/accuracy, sensitivity, and completeness have been met, and whether the calculation of concentrations based on instrument responses and other factors is accurate. The researcher will conduct validation. No independent third party data validation will be conducted for this project.

After data verification and validation are completed, staff will enter all field and laboratory data into a file labeled FINAL. Another staff member will independently review the data for errors at an initial 10% frequency. If the staff member discovers any significant entry errors, he/she will conduct a more intensive review.

**Data Quality (Usability) Assessment**

The researcher will examine the complete data package to determine whether the data meet required reporting limits. If portions of the data do not meet these limits, the project manager will assess the data in terms of its usability to meet the study objectives. The WSC researcher will consider any data qualifiers in evaluating the usability of the data for both evaluating runoff samples and the leachate samples.

Based on the design of the study, the WSC researcher envisions the following analyses in either tabular or graphical format, depending on the usability of the data.

• Evaluation of median and ranges of chemical parameters for each roofing panel over the timeframe of the study.
• Assessment of the aerial deposition (wet and dry) on the two control panels and comparison with the wet deposition on the stainless steel panel.
• Assessment of contaminant concentrations (minus the aerial deposition) on an event by event basis for each panel type.
• Assessments of potential impact of rain intensity on contaminant concentrations within roofing types, if an adequate range of intensities is available.
• Comparison of the results of runoff from the three replicate asphalt shingle panels without AR.
• Results of the toxicity analysis for each of the two species (*C. dubia* and zebra fish) for which toxicity is assessed from each of roofing materials and glass controls.
• Results of the toxicity analysis for the coho salmon for the three selected roofing material types and the glass control.
Audits and Reports

Audits
ARI participates in performance and system audits of their routine procedures. The public may request results of these audits in writing.

Chemical Data Reporting
The WSC researcher will prepare a draft and final report in accordance with the schedule in Table 3. The report will include the following assessment of the analyses of runoff for the chemical parameters:

- Description of field and laboratory methods.
- Deviations from this QAPP.
- Photographs of the roofing panel setup.
- Sample information such as precipitation intensity, duration and depth, dates, times, and results of chemical analyses.
- Reported analytical results for the control panels representing wet and dry aerial deposition.
- Reported analytical results will be adjusted by subtracting the values represented by aerial deposition for each rain event.
- Summary of all adjusted results. The summary will include descriptive statistics such as median values.
- Comparisons of study data with literature values including Winters et al 2014.
- Summary and statistical analysis for each of the toxicity tests for differences from controls.
- Comparison of toxicity results to relevant published values for runoff from other roofing studies.
- Discussion of data quality and the significance of any problems encountered in the sampling or analysis.
- Conclusions that can be drawn from the study and recommendations for future studies.
- Raw data provided in digital form in appendices.

WSC reviewers will comment on a draft of the report. Comments will be addressed before the RTF members receive a copy of the draft report for their review and comment. The researcher investigator will address comments and prepare the final investigative report. WSC will provide public access to electronic versions of the report generated from this project via WSC’s internet homepage (http://www.wastormwatercenter.org/). The data generated will be stored in EXCEL files and be available upon request at the end of the project.
References

http://arilabs.com/?wpfb_dl=10

http://arilabs.com/?wpfb_dl=5


https://fortress.wa.gov/ecy/publications/SummaryPages/1303105.html


https://fortress.wa.gov/ecy/publications/summarypages/1103024.html

https://fortress.wa.gov/ecy/publications/summarypages/1103055.html


Appendix A. Roofing Assessment Procedures

Decontamination Procedures

Panels
Following relocation of the roofing panels in 2014, panels have been exposed continuously the weather conditions and the aging process. Panels will not be decontaminated (rinsed with distilled water) as they were originally after construction. Further, the panels will not be rinsed between rain events.

Gutters
The Teflon®-lined HDPE gutters have been stored at the WSC facility since their relocations. They will be decontaminated initially using the following procedure. The gutters will be washed with a Liquinox detergent solution, rinsed with each of the following sequentially: three rinses with tap water, a 10% nitric acid rinse, three laboratory-provided distilled deionized water rinses, and a pesticide-grade acetone. The gutters will be allowed to air-dry before obtaining an equipment rinse blank by combining a distilled water rinse from three gutters to ensure they are properly cleaned. Gutters will be wrapped with aluminum foil until they are placed outdoors.

Following sampling of a rain event, the gutters will be rinsed three times with distilled deionized water. Rinse water will be discarded on the ground. The gutters will remain open to the air between rain events. Results will be adjusted for aerial deposition that lands in the gutters by subtracting concentration results collected from the control panel.

Stainless-Steel Runoff Containers, Mixer, and Pump Tubing
All stainless-steel runoff collection containers and Teflon® tubing, and silastic tubing (internal to the peristaltic pump) will be dedicated to a roofing panel type throughout the course of the study. Prior to sampling, all equipment will be thoroughly decontaminated. All stainless-steel sampling gear (56-liter stainless-steel runoff collection containers, mixing device and measuring device), the stainless steel roofing panel, and Teflon and silastic tubing will be cleaned by washing with Liquinox detergent, followed by three sequential rinses with tap water, a 10% nitric acid rinse, a deionized water rinse, and a pesticide-grade acetone rinse. The equipment will then be air-dried and wrapped in aluminum foil (dull side in). The stainless steel panel will be stored indoors to prevent accumulation of dry aerial deposition.

Prior to a sampling event, an equipment rinse will be obtained from the equipment using laboratory-provided distilled deionized water. Equipment rinse water from all equipment will be combined into a single equipment rinse blank.

Between each sampling of the runoff from each panel, the mixing device and the measuring device will be rinsed with three rinses of tap water, a 10% nitric acid rinse, a pesticide-grade
acetone rinse, and five rinses with distilled deionized water. The nitric acid and acetone will be collected, and managed as hazardous/dangerous waste. Water rinses will be discarded onto the ground.

All sampling and handling activities will be conducted by personnel wearing non-talc nitrile disposable gloves. Staff will ensure that only clean hands will touch the clean equipment. Gloves will be changed often, as appropriate, to prevent contamination and, at a minimum, between sampling runoff from each type of panel.

**Stainless-Steel Runoff Panel**

The stainless steel panel used for sampling pure rain water, will be decontaminated using the same procedures as the stainless steel containers. After decontamination and air drying, it will wrapped in aluminum foil. It will be deployed to its field location immediately prior to the first rain event. After each rain event, it will be triple rinsed with distilled deionized water, air dried and covered with non-plastic fabric to prevent dry aerial deposition. Prior to a sampling event the non-plastic fabric will be removed. The purpose of this panel is to collect runoff for chemical analysis which reflects wet deposition and rain water quality.

**Glassware for Toxicological Analysis**

Glassware used for toxicological analyses will be decontaminated by washing it with simple green, cleansed in tap water for a minimum of three rinse cycles and then rinsed under a hood three times in acetone and methylene chloride. Clean glassware will be allowed to air dry under the hood.

**Sample Labeling**

Each sample will have a unique, 11-digit, alpha-numeric identification number. The number will consist of three alphabetical numeric characters that represent the roofing type, 6 numeric digits representing the date, and two digits that represent sample number. For example, a sample collected from the Zincalume® roof, on November 24, 2012, from the sample of a rain event would be labeled as follows:  
ZIN-11-24-12-01

For a replicate sample the numbers would be recorded as follows:
- ZIN-11-24-12-01 (field notebook would record sample taken at 9:15)
- ZIN-11-24-12-02 (field notebook would record field split taken at 9:25)
- ZIN-11-24-12-03 (field notebook would record MS taken at 9:35)
- ZIN-11-24-12-04 (field notebook would record MSD taken at 9:45)

Each sample that is couriered to the laboratory will have a sample label with the following information clearly printed in indelible ink:
- Unique sample number
- Date of sample collection
- Time of sample collection (using a 24-hour clock)
- Analyses required
- Sample preservation (if any)
• Initials of the field crew member who collected the sample

Sample Collection
Rain events may be sampled when precipitation volume generates adequate sample volume (not less than 0.08 inch or 5.2 liters). If sample volume is approaching the maximum collection container volume, staff will record the time, and quickly remove gutters from the apparatus, ceasing runoff collection. Sample collection containers will not be allowed to overflow. Sampling may occur 7 days a week, 24 hours a day.

For each rain event, samples will be collected using the following procedures conducted at each panel:

1. Prior to deploying the equipment outdoors, obtain a composite sample of the final rinse from the stainless-steel containers, Teflon® and silastic tubing, mixing device, and measuring device. Ensure at least 3 liters of rinsate for equipment rinse samples. Pump equipment rinse samples into the pre-cleaned laboratory sample bottles (one for each metals, PAHs and phthalates.) Label the sample bottles and record the sample number and other data in the field notebook. Place the samples in a cooler where the field samples will be stored for later transport to the laboratory. Add the equipment rinse samples to the chain of custody forms.

2. Calibrate the pH meter and the specific conductance meter per Ecology SOPs EAP031 and EAP032, respectively (Ward, 2006 and 2011).

3. Label the sample bottles as described above.

4. Don a new set of nitrile gloves.

5. Remove the measuring device from the aluminum foil, touching it only with clean gloved hands. Record the volume of water collected from each roof panel based on the depth of the collection pot using 1-cm hatch marks on the stainless-steel rod.

6. Remove the panel-specific tubing from the foil, setting it on the inside of the foil.

7. Open the head of the peristaltic pump and place the silastic tubing in it. With clean gloves attach the Teflon® tubing to each end of the silastic tubing.

8. Remove the mixing device from the foil, using clean gloved hands. Attach the mixing device to the Teflon® tubing. Using a continuous motion, mix the contents of the stainless-steel container by raising and lowering the mixing device without breaking the surface at a rate of approximately 9 inches per second for at least 1 minute prior to turning on the pump.

9. Continue mixing, while a second staff person removes the sample bottle cap with clean gloved hands. The second staff person will turn on the pump with one hand. The first person will allow approximately 25 ml to run onto the ground to eliminate potential tubing contamination before inserting the effluent end of the Teflon® tubing into the top of the laboratory pre-cleaned sample bottle. Fill sample bottle. Avoid collecting debris such as leaves in the sample.

10. Fill each sample bottle to full, but not overflowing.

11. Recap the sample bottle tightly.

12. If the sample bottle is glass, wrap it in bubble wrap and place it in the cooler.

13. Where split samples or QA samples are required, mix the stainless-steel runoff collection container until all samples have been obtained.
14. In the field, create dissolved water blank samples by pouring laboratory-provided distilled water into the sample bottle (one for each metals, PAHs and phthalates). Label the sample bottles and record the sample number and other data in the field notebook. Place the samples in the cooler with the field samples for subsequent transport to the lab. Add the samples to the chain of custody forms.

15. Fill a cup with sample from the stainless-steel container to measure pH using the protocols in EAP031 (Ward, 2006) and specific conductance using the protocols in EAP032 (Ward 2011). Measure and record the pH and specific conductance of the sample.

16. When all sampling of all panels has been completed, squirt at least 1/4 liter of laboratory-provided distilled water through each gutter to wash out any accumulated particulates.

17. After sampling each panel, decontaminate the measuring stick and mixing device as described in the decontamination procedures. Place them on a non-contaminated surface such as aluminum foil.

When all the panels have been sampled:
1. Download precipitation data from data logger.
2. Check all bottle labels, complete the chain of custody forms (see below), pack up the coolers, add ice, and move the coolers to a refrigeration unit, if they will not immediately be transported to the laboratory.
3. Move all of the sampling equipment into the cleaning room and decontaminate the sampling equipment as described above.
4. Cover all decontaminated equipment in aluminum foil.

**QA Samples and Blanks**

**Blank Samples**
The following blank samples will be obtained for each sampling event:

- A distilled water blank will be obtained in the field using the procedure described above. This sample will be analyzed for dissolved metals, PAH and phthalates.

- One initial equipment rinse blank will be obtained as described above. The equipment rinse blank will be analyzed for dissolved metals, PAHs and phthalates.

**Other QA Samples**
The following QA samples (as enumerated in Table 11) will be obtained for each sampling event:

- Field splits
- Asphalt shingle replicates
- MS/MSDs

**Sample Packing and Shipping**
Samples collected for laboratory analysis will be labeled, packed and shipped as follows:
1. Ensure the sample bottle is labeled and logged in the field notebook, and recorded on the chain of custody (CoC).
2. Place each sample in a Ziploc bag. For those sample bottles that are glass, pre-wrap in bubble wrap.
3. Pack the bottles in insulated ice chests with either gel ice or crushed ice that is double-bagged in closed Ziploc plastic bags.
4. Maintain the temperature in the ice chest at 6 °C ± 2°C.
5. Complete a chain of custody form for those bottles in each packed ice chest. Place the CoC in a plastic closed Ziploc bag and tape it to the inside lid of the ice chest. All samples will be in the control of the field crew or laboratory personnel until they are delivered to the laboratory.
6. Call the courier from ARI to let him know to transport the sample to the laboratory (at address below) on the next weekday.

Analytical Resources, Inc.
4611 S. 134th Place, Suite 100
Tukwila, WA 98168-3240
(206) 695-6200

**Chain of Custody Forms**

Chain of custody (CoC) forms developed for this project will be used for samples submitted to the laboratory for analysis. An example of the CoC form is provided at the end of this appendix. The CoC must contain the following information for each sample:

- Unique sample number
- Date and time of sample collection (using a 24-hour clock)
- Matrix
- Number of sample containers
- Analyses required
- Signature of field crew member with responsibility for ensuring custody of samples
- Signature of person at laboratory receiving samples
- Contract information for person receiving data
- Date results are needed (not more than 10 business days after laboratory receipt)

The laboratory-signed, completed CoC will be scanned and emailed to the WSC researcher upon receipt by the laboratory and with the data package.

**Field Notebook Records**

All records of the project will be maintained in a waterproof field notebook. The following information shall be recorded for each field rain event:

- Calibration records of pH meter and specific conductance meter each day of use
- Date and time rain began
- Date and time rain stopped
- Calculated rain duration
- Rain intensity (mm/hr) downloaded from the rain gauge data logger
- Calculated rain depth (mm) downloaded from the rain gauge data logger
- Depth and calculated volume of runoff collected from each roof type
- Measured pH and specific conductance of runoff collected from each roof type
- Name of samplers
- Unusual observations about the event
- Unusual observations or procedures at each sample station (panel)
- Sample identification number for each sample (field replicate, MS, MSD, equipment rinse sample, and laboratory water blank) taken with description and time each sample bottle was filled
- Time samples were moved into a cooler for transport to the lab.

If a correction is required, a single line will be drawn through the incorrect datum, and the correct datum will be written above. The correction will be initialed. Each page of the field notebook will be dated and signed by the person completing the entries. If a partial page is left blank, a diagonal line will be drawn through the blank portion of the page, and it will be dated and signed.

At the end of each rain event, the field notebook will be reviewed by the second field crew person (i.e., the person not doing the recording). Corrections will be made or omissions added during the review as described above.

Each day in which recordings in the field notebook are made, the pages completed that day will be scanned and emailed to the WSC researcher.

**Re-Deployment**
At the end of each rain event, the stainless-steel containers, panel, mixing device, and tubing will be decontaminated as described above. The equipment will be wrapped and stored. Weather reports will be reviewed daily to determine: (1) whether 6 hours with less than 0.1 inch of precipitation has elapsed since the preceding event, and (2) whether a rain event of sufficient size is predicted. Based on best professional judgment of the staff and these two criteria, the stainless-steel containers will be re-deployed to catch the first flush of the next event.

**Maintenance of Pilot Roofing Area**
No gasoline-powered equipment is permitted to be used to maintain any of the landscaping around the roofing panels. The area will be allowed to grow when sampling is not being conducted. Staff will monitor vegetation growth in the area surrounding the roofing panels monthly. Staff will maintain the vegetation using hand-held equipment (such as electric weed-eater, clippers, or a scythe), as necessary to keep vegetation from growing on or over the panels or the equipment. Staff will ensure that no residual vegetation lands on the roofing panels.
**Laboratory Toxicological Procedures**

WSU staff will follow the procedures described by McIntyre et al., 2015 to assess runoff toxicity in *C. dubia*, McIntyre et al., 2014 to assess runoff toxicity in zebra fish and coho salmon. For the coho salmon toxicity analyses, a 50% or greater dilution may be necessary if the volume available from the rain event sampled is not sufficient for the test.
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**Limits of Liability:** ARI will perform all requested services in accordance with appropriate methodology following ARI Standard Operating Procedures and the ARI Quality Assurance Program. This program meets standards for the industry. The total liability of ARI, its officers, agents, employees, or successors, arising out of or in connection with the requested services, shall not exceed the invoiced amount for said services. The acceptance by the client of a proposal for services by ARI releases ARI from any liability in excess thereof, notwithstanding any provision to the contrary in any contract, purchase order or co-signed agreement between ARI and the Client.
## Appendix B. Estimated Analytical Costs

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