

Quality Assurance Project Plan

Roofing Materials Assessment: Investigation of Toxic Chemicals in Roof Runoff

January 2013 Publication No. 13-03-105

Publication Information

Each study conducted by the Washington State Department of Ecology (Ecology) must have an approved Quality Assurance Project Plan (QAPP). The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completing the study, Ecology will post the final report of the study to the Internet.

This study has been funded in part by the United States Environmental Protection Agency (EPA) through their National Estuary Program (NEP), via an interagency agreement (PC-00J20101) with Ecology serving as Lead Organization for "Toxics and Nutrients Prevention, Reduction, and Control" projects. This QAPP is available from Ecology's website at https://fortress.wa.gov/ecy/publications/SummaryPages/1303105.html, as will be the final project report. The contents of these documents do not necessarily reflect the views and policies of the EPA, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Data for this project will not be available on Ecology's Environmental Information Management (EIM) website as stormwater runoff data from this study are not considered environmental data.

Ecology's Activity Tracker Code for this study is 13-003.

Author and Contact Information

Nancy Winters P.O. Box 47600 Environmental Assessment Program Washington State Department of Ecology Olympia, WA 98504-7710

For more information contact: Communications Consultant, phone 360-407-6834.

Washington State Department of Ecology - www.ecy.wa.gov

- Headquarters, Olympia 360-407-6000
- Northwest Regional Office, Bellevue 425-649-7000
- Southwest Regional Office, Olympia 360-407-6300
- Central Regional Office, Yakima 509-575-2490
- Eastern Regional Office, Spokane 509-329-3400

Any use of product or firm names in this publication is for descriptive purposes only and does not imply endorsement by the author or the Department of Ecology.

If you need this document in a format for the visually impaired, call 360-407-6834. Persons with hearing loss can call 711 for Washington Relay Service. Persons with a speech disability can call 877- 833-6341.

Quality Assurance Project Plan

Roofing Materials Assessment: Investigation of Toxic Chemicals in Roof Runoff

January 2013

Approved by:

Signature:	Date: January 2013
Andrew Kolosseus, Client, Reducing Toxic Threats, W2R	
Signature:	Date: January 2013
Carol Kraege, Client's Section Manager, W2R	
Signature:	Date: January 2013
Nancy Winters, Author / Project Manager / Principal Investigator, EAP	
Signature:	Date: January 2013
Allison Kingfisher, BMS/Facilitator, W2R	
Signature:	Date: January 2013
Dale Norton, Author's Unit Supervisor, EAP	
Signature:	Date: January 2013
Will Kendra, Author's Section Manager, EAP	
Signature: Joel Bird, Director, Manchester Environmental Laboratory	Date: January 2013
Joer Bild, Director, Manchester Environmental Laboratory	
Signature:	Date: January 2013
Bill Kammin, Ecology Quality Assurance Officer	
Signatures are not available on the Internet version.	
RMS: Building Materials Specialist	

BMS: Building Materials Specialist W2R: Waste 2 Resources Program

EAP: Environmental Assessment Program

Table of Contents

	Page
Table of Contents	2
List of Figures and Tables	4
Abstract	5
Background	6
Project Description Roofing Task Force Involvement	8
Roofing Task Force Issues of Future Concern Objectives Summary of Project	13
Organization and Schedule Training	
Quality Objectives Sensitivity	18
Representativeness Precision	19
Bias/Accuracy Comparability Completeness	20
Study Design	24
Roofing Types and Products Pilot-Scale Roofing Panels	25
Monitoring and Predicting Rain Events Rain Event Definition and Number Analyses	27
Leaching Procedure	31
Sampling Procedures	33
Measurement Procedures	35
Quality Control Procedures Field Quality Control Laboratory Quality Control	36
Data Management Procedures	
Data Verification and Validation	
Data Quality (Usability) Assessment Pilot Roofing Study SPLP Leaching Study	39
Audits and Reports	40

Data Reportin	ıg	.40
References		.42
Appendices		.45
Appendix A.	Literature Review	.46
Appendix B.	List of Roofing Task Force October 24, 2012 Meeting Participants	.63
Appendix C.	Roofing Assessment Procedures	.66
Appendix D.	Estimated Analytical Costs	.75
Appendix E.	Modifications to EPA Method 1312, Synthetic Precipitation	
	Leaching Procedure	.78
Appendix F.	Glossary, Acronyms and Abbreviations	.79

List of Figures and Tables

Figures	U
Figure 1. Conceptual model of project roles	9
Figure 2. Illustration of pilot-scale roofs.	26

Tables

Table 1.	Estimated release of selected chemicals from roofing in the Puget Sound basin
Table 2.	Roof types selected for analysis
Table 3.	Organization of project staff and responsibilities15
Table 4.	Proposed schedule for completing field and laboratory work, and reports16
Table 5.	Measurement quality objectives for total recoverable and dissolved metals21
Table 6.	Measurement quality objectives for PAHs
Table 7.	Measurement quality objectives for phthalates and PBDEs23
Table 8.	Percent of roof surface area in the Puget Sound basin represented by each roof type
Table 9.	Analyses by roofing type for each of the first three rain events29
Table 10	. Analyses by roofing type for each of the remaining rain events
Table 11	. Replicates of roofing coupons for analyses of SPLP leachate32
Table 12	. Sample bottles, preservation, and holding times
Table 13	. Numbers of samples by analysis per rain event for first three and remaining sampling events of the pilot-scale roof runoff study
Table 14	. Laboratory quality control samples for pilot-scale roof runoff study37
Table 15	. Laboratory quality control samples for SPLP leaching study

Abstract

The Washington State Department of Ecology (Ecology) assessed potential sources of toxics entering Puget Sound and found that roofing materials may be sources of arsenic, copper, cadmium, zinc, and possibly PAHs and phthalates in the Puget Sound basin (Ecology, 2011a and b). However, the assessment used literature values from locations across the U.S. and the world to represent contaminant concentrations. A number of regional factors such as precipitation intensity, duration, pH, and materials used could have a significant impact on the release of contaminants from roofing materials, and thereby affect Ecology's earlier assessment.

The Environmental Protection Agency is funding Ecology to examine these regional factors by conducting a pilot assessment of roofing materials in the Puget Sound basin. National Estuary Program (NEP) funds will also help Ecology form a Roofing Task Force to provide input on the study design and follow-up actions based on the study results. Based on 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 located at the Ecology Headquarters building in Lacey, Washington. The project will collect samples from up to 10 rain events from each panel and analyze them for a variety of contaminants including five metals, polycyclic aromatic hydrocarbons, phthalates, and polybrominated diphenyl ethers. In addition, the project will evaluate samples of certain roof materials exposed to a leaching procedure to determine coatings' effectiveness in reducing contaminants of concern. The study will inform future roofing investigations.

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.

Background

Researchers have studied the contribution of contaminants from roof runoff to stormwater for over two decades. The predominant focus of much of the research has been the contribution of heavy metals from roofing materials into stormwater runoff, which may subsequently enter rivers and streams (Bannerman et al., 1983; Boller, 1997; Steuer et al., 1997; Good, 1993; Yaziz et al., 1989). These metals may adversely affect aquatic life.

While wet and dry air deposition contributes to the contaminants from commercial, residential, and industrial roofs, Pitt et al. (2000) demonstrated that metals, polycyclic aromatic hydrocarbons (PAHs), phthalates, and other compounds leach from roofing and other construction materials. Recent field studies have attempted to control for the contribution of air deposition to evaluate the concentrations leaching from the roofing materials. Appendix A provides a summary of the literature associated with contaminants from roofing runoff, including the impacts of material composition, angle of roof inclination, roof length, and conditions, such as rain pH, intensity, duration, depth, and prevailing wind conditions on runoff quality.

A recent assessment of the anthropogenic sources and annual releases of toxic chemicals to the Puget Sound basin indicated that roof runoff could be a major contributor of certain metals and comparatively minor sources of phthalates and PAHs (Ecology, 2011a). Ecology obtained information from many sources on chemical concentrations used to derive these estimates. Primary resources were: published, peer-reviewed literature peer-reviewed literature, government and non-governmental organization publications, government databases, direct communications with experts, readily available marketing data, and other miscellaneous information resources. Table 1 summarizes the concentration ranges used for the loading study. Appendix B of the Ecology study (2011a) describes in detail how concentrations were used to derive loadings using roof types, footprints, and land use data for the Puget Sound region.

The role that chemical loads from roof runoff play in creating hazards to aquatic organisms is difficult to define and may depend largely on the geographical scale being evaluated. One can readily compare chemical concentrations in roof runoff, such as those shown in Table 1, to various thresholds established to protect aquatic organisms and human health.

	Est. Range of	Estimated Annual Release	Contribution to		
Chemical	Concentrations	in the Puget Sound Basin	Total Anthropogenic		
	(ug/l)	(t/yr)	Release		
Arsenic	-<0.01 - 1.43	< 0.01 - 0.84	19%		
Cadmium	0.24 - 1.9	0.5 - 0.7	53 - 68%		
Copper	4 - 1,850	12 - 43	3% - 29%		
Lead	< 0.1 - 52	15 - 20	2% - 12%		
Zinc	24.6 - 16,317	210 - 2,800	37% - 97%		
PAHs	0.61 - 2.06	0.6	0.02%		
Bis (2-ethylhexyl) phthalate	а	0.14	<1%		

Table 1.	Estimated release of	of selected chemical	s from roofing in	the Puget Sound basin.
----------	----------------------	----------------------	-------------------	------------------------

Source: Ecology, 2011a

^a Annual release based on amount of PVC and non-polymers used in Washington (Ecology 2011a)

However, concentrations of contaminants in roof runoff are expected to be attenuated by many mechanisms (e.g., deposition, transformations, and uptake) before reaching waterbodies and becoming available to aquatic life forms. Characterizing attenuation becomes more difficult as geographic scale increases. At a stream sub-basin scale, assigning metals contribution to roof runoff becomes difficult since other chemical sources must be considered as well as environmental transport and attenuation factors. An example of the difficulties in doing this was demonstrated by Paulson et al. (2011) when he attempted to conduct a copper mass-balance in two small urban sub-basins.

At a regional scale, the linkages between chemical sources and receiving water concentrations become even more tenuous. Based on information generated in the reports on sources and assessment of chemicals in the Puget Sound basin (Ecology, 2011a and 2011b), the following generalized conclusions may be drawn related to chemicals found in roof runoff and chemical hazards in general.

- 1. Release estimates suggest that arsenic, cadmium, copper, lead, and zinc in roof runoff may be among the most significant anthropogenic releases of these metals in the Puget Sound basin.
- 2. A substantial portion of copper concentrations observed in fresh and marine waters regionwide are at levels where adverse effects to aquatic organisms are documented (Ecology, 2011b).
- 3. The same appears to be true for zinc in marine waters; arsenic, cadmium, copper, and bis (2-ethylhexyl) phthalate (DEHP) in freshwater sediments; and DEHP in marine sediments and freshwater and marine seafood (Ecology, 2011b).

Based on these generalized conclusions, it appears that gaining a better understanding of regionspecific information on contaminant levels in roof runoff from various roofing materials is warranted. Currently available information is insufficient to provide annual release estimates with a high degree of certainty due to:

- A lack of region-specific data for Puget Sound.
- Few studies controlling for factors such as concentrations of contaminants in atmospheric deposition.

This study focuses on obtaining the region-specific information from one component of roofing systems, the roofing materials. Ecology recognizes that roofing systems are complex and include not only the roofing materials, but also components such as gutters and downspouts, HVAC systems, flashings, and exposed fasteners. This pilot study takes a systematic approach to the study by assessing only specific types of roofing materials (those most commonly used in the region) and by controlling as many variables as possible.

Project Description

This study intends to provide initial information needed to evaluate whether roofing materials are a potential source of toxic chemicals in the Puget Sound basin. This study will assess the concentrations of a number of chemicals of concern released from roofing materials during precipitation events. In 2012, Ecology convened a Roofing Task Force (RTF) of manufacturers, contractors, and other stakeholders to provide input to the design of this study. The RTF's input is described in the next section.

This study is Ecology's initial investigation specific to roofing materials and as such serves as a pilot study. The study will not recommend specific products for use by the roof manufacturing community, construction contractors, roofing designers, homeowners, or others. In addition the results are not intended for making decisions or recommendations for treatment practices to reduce toxic chemicals in roof runoff. Results of this study are intended to help guide Ecology and the RTF in making recommendations for follow-up actions and investigations to understand the role of roofing systems in releasing toxics within the Puget Sound basin.

Roofing Task Force Involvement

The design of this study includes input from an RTF of manufacturers, contractors, roofing associations, and other stakeholders. Figure 1 depicts the conceptual model of the study and the role of the RTF. This flowchart illustrates steps to be conducted by the Ecology Technical Lead for the project (oval). The figure also describes the Technical Lead's relationship with the Building Materials Specialists (BMS) and the RTF, who will provide input (rectangles) to the study design and review of the report. Triangles represent steps to be conducted by Ecology staff or contractor. The tasks detailed in subsequent sections generally include only Technical Lead (project manager) responsibilities. The flowchart shows Ecology relationships with the BMS and the RTF since they will affect the project schedule, but tasks associated with their roles are not shown.

RTF members were solicited through associations and roofing manufactures. In September a small group was convened to request names of additional associations, manufactures, and governmental and non-governmental participants that had not been identified by Ecology. Ecology staff contacted these associations and invited them to the first official RTF meeting in October 2012. Additionally, as the project has progressed, associations have identified other potential members who ultimately joined the meetings.

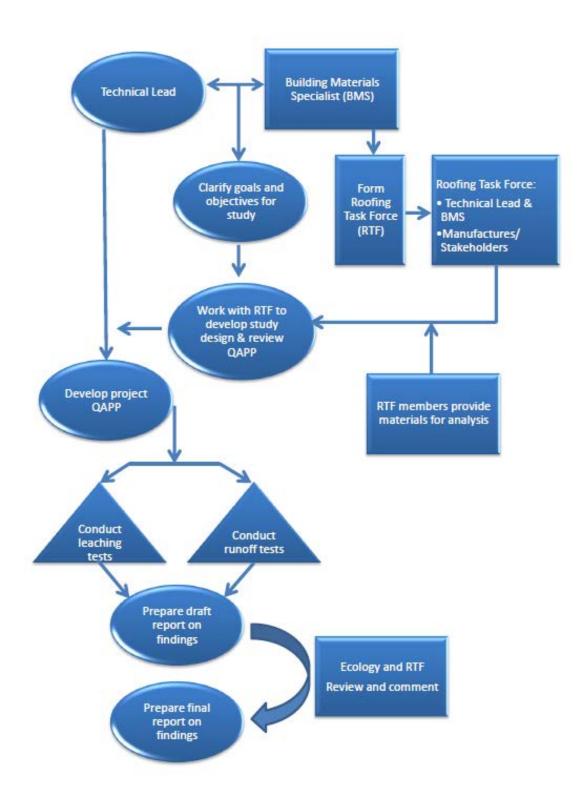


Figure 1. Conceptual model of project roles.

The RTF met on October 24, 2012. The list of participants in that meeting, as a subset of all members who have participated, is provided in Appendix B. After briefly describing the Puget Sound Toxics Assessment studies (Ecology 2011 a and b) and the objectives of the study, Ecology asked participants to provide input on the design of the study, the chemicals of concern, and the types of roofing to be evaluated.

Three design options for the study were presented for the RTF's initial consideration and discussion of advantages, disadvantages, and considerations. One of the RTF members suggested a fourth option. The options included:

- Option 1 Test panels outdoors (field). Exposure of pilot-scale panels of roofing material to same rain conditions at a single location (e.g., the Ecology building).
- Option 2 Test panels exposed to simulated rain event (laboratory). Exposure of pilot-scale roofing material to simulated rain from a rain maker (controlling rain chemistry and precipitation duration, intensity, depths).
- Option 3 Leaching tests. Exposure of small samples of roofing material to slightly acidic water for 18 hours (laboratory). This would be a modified Synthetic Precipitation Leaching Procedure (SPLP) (EPA method 1312).
- Option 4 Field study. Collection of roof runoff from existing roofs throughout the Puget Sound basin.

In general, the meeting participants favored a pilot-scale field study (Option 1), with the hope that the field panels could be used in subsequent studies to assess the impacts of other factors, including aging, that may affect runoff quality.

For the near term, Options 2 and 4 have not been considered for this study for a number of reasons. Option 2 was eliminated because of the difficulties and expense of constructing a rainmaker without introduction of the plasticizers and metals that are of concern to the study. Option 4 would take into account entire roofing systems, but it would introduce a multitude of variables, such as precipitation variability from area to area, unknown roof manufacturing processes, additional construction and/or repair materials, and unknown roof age. Additionally, the U.S. Environmental Protection Agency (EPA) is providing a grant to the Port Townsend Marine Science Center to assess runoff from residential roofs in the Puget Sound basin (Walat, pers. comm., 2012), which should provide a good comparative study.

Option 3 may be useful for comparing concentrations of contaminants of concern leaching from roofing materials with and without applied post-manufactured coatings. While the leaching process does not simulate the wet and dry cycles of precipitation events in the Puget Sound basin, its study may be useful for assessing relative effectiveness in reducing metals concentrations in runoff from metal roofing. A small leaching study will be included in this study, as resources allow.

The RTF participants were asked to recommend up to 15 roofing types that the study should assess. The maximum number of roofing types that could be assessed was based on available funding. To guide the discussion, Ecology provided data used in the Puget Sound Toxics Assessment (Ecology 2011a), including a list of roofing types representing more than one percent of the roof surfaces in the Puget Sound basin as described in the study. To this list the participants added newer and emerging roofing technologies. Additionally the RTF provided input on the roofing materials considered in this study through their comments on the QAPP. Table 2 lists the roofing types that will be evaluated for this study and represents more than 98 percent of the roof surfaces that Ecology's 2011 report found to be used in the greater Puget Sound basin (Ecology 2011a).

Following the October 24, 2012 meeting, Ecology spoke with numerous manufacturers concerning the composition of their roofing materials, to gain an understanding of the composition of various types of roofing materials. Ecology encouraged manufacturers to provide them with chemical composition information. If appropriately requested by the manufacturers, proprietary portions of this information submitted by the manufacturers will be kept confidential. Based on a review of available information and information provided by RTF members, not all roofing types may include the same chemicals of concern. Thus, not all of the roofing types will be analyzed for the same constituents in the runoff for all sampling events. The details of the sample design are provided in the Sampling Process Design section.

No.	Roof Type	Description/Comment						
	Steep Slope Roofs							
1	Asphalt shingle - composite 6 types of shingles without algal resistant (AR) copper-containing granules	A composite of 6 different asphalt manufacturers' shingles commonly used in Washington without chemicals used for algae control						
2	Asphalt shingle - composite 6 types of shingles with AR copper-containing granules	A composite of 6 different asphalt manufacturers' shingles commonly used in Washington with chemicals used for algae control						
3	Copper	Copper roofing panel						
4	Manufacturer-painted galvanized steel	Galvanized steel coated with paint applied by the manufacturer						
4	Concrete tile	Concrete tile is generally 20-30% concrete; 50-60% sand and aggregate; 0-5 % limestone and may include an acrylic coating						
6	Wood shingle/shake	Cedar most prevalently used in Washington, with no preservative and no fire retardants						
7	Manufacturer-treated wood shingle/shake	Treated with chromate copper arsenate (CCA) to preserve wood						
8	Frosted glass (control)	Steep slope control to subtract wet and dry air deposition						
	Low S	lope Roofs						
9	Thermoplastic polyolefin (TPO)	A single ply thermoplastic roofing material						
10	Polyvinyl chloride (PVC)	A single ply roofing material						
11	Ethylene propylene diene monomer (EPDM)	A rubberized single ply roofing material						
12	Built-up roof (BUR) with oxidized asphalt granulated cap sheet	Standard commercial roofing includes asphalt felt and hot applied asphalt and an oxidized asphalt granulated cap						
13	Modified BUR with styrene butadiene styrene (SBS) granulated cap sheet	Standard BUR with SBS added as cap						
14	Modified BUR with Atatic polypropylene (APP) granulated cap sheet	Standard BUR with APP added as cap						
15	Zincalume®	An aluminum zinc alloy product that represents a high fraction of the sheet metal roofing market in Western Washington						
16	Frosted glass (control)	Low slope control to subtract wet and dry air deposition						

Table 2. Roof types selected for analysis.

Roofing Task Force Issues of Future Concern

At the October 24, 2012 meeting, the RTF discussed a number of variables that should be studied. In their comments on the draft QAPP, some RTF members and associations also recognized variables that required further study. While these variables have not been included in this study because of the limitations defined by available resources, they are listed here for consideration in future studies. The list below has not been prioritized by the RTF.

- Evaluation of the leaching of materials over their life span, assuming that materials may leach a greater amount and number of constituents as they age.
- Evaluation of common components of roofing systems, such as the effects of the composition of heating, ventilation, and air conditioning (HVAC) systems, gutters and downspouts, and flashing materials. An evaluation of each of these components is a study in and of itself, and beyond the scope of this project.
- Evaluation of the impacts to stormwater of "after-market products." These are products that building owners or their contractors apply to roofing materials for maintenance and repair, such as algae/moss removal treatments, post-manufactured treatments or coatings, adhesives and seaming tapes used for repair. The RTF noted that we should not eliminate constituents from the manufacture of roofing materials that would subsequently require greater maintenance with application of products that could result in greater environmental harm.
- Evaluation of the components of vegetated roof systems, underlayments and barrier systems, and soil matrices.
- Evaluation of the leachability of organic biocides from roofing materials manufactured with these products.
- Evaluation of runoff from replicate panels of each type over multiple rain intensities to allow for statistical analysis of the results.
- Analysis of the aquatic toxicity of roofing runoff.
- Evaluation of the fate and transport of contaminants after they leave the roofing materials.

Pending the findings of this study, these tabled evaluations should be considered in future efforts.

Objectives

This study is designed as a 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 study are to:

- Determine the range of concentrations of specific chemicals leached from various roofing materials used in the Puget Sound basin by analyzing runoff from various roofing materials.
- Determine the range of loadings of specific chemicals leached from various roofing materials on a per unit area basis and on a per unit area and precipitation depth basis.

• Determine whether roofing materials leach at different rates with different precipitation intensities, durations, or volumes (rain depth over a unit area).

A secondary objective of this study is to determine whether post-manufactured coatings can reduce the leaching from specific roofing materials. Achieving this objective is dependent on available resources.

Ecology recognizes a number of limitations of the study based on available budget. These include but are not necessarily limited to evaluation of:

- Roofing materials only rather than roofing systems
- New materials only
- Replicates for asphalt shingle roofs only
- A short samples 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 18 constructed pilot-scale roof panels including two glass controls. All pilot panels will be the same size and will be 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 constructed and sampled. Each of these samples 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 2 lists the types of roofing materials that will be evaluated.

Ecology will place the pilot project roofing assemblages in a secure location at the Ecology headquarters facility in Lacey, Washington. This location will ensure that all panels are exposed to the same precipitation event and the same wind direction simultaneously.

Ecology will analyze runoff from roof panels from up to 10 rain events between February and the end of May 2013. Ecology will analyze all runoff samples for metals (arsenic, cadmium, copper, lead and zinc), PAHs, phthalates, and polybrominated diphenyl ethers (PBDEs) for the first three rain events and a more limited list for the remaining storm events, as described subsequently.

In addition, leaching tests will be used to assess the relative effectiveness of post-manufactured coatings in reducing constituent leaching from metal roofs.

Organization and Schedule

Table 3 lists the people involved in this project. All are employees of Ecology. Table 4 presents the proposed schedule for this project.

Staff	Title	Responsibilities
Andrew Kolosseus RTT, W2R Phone: 360-407-7543	EAP Client	Clarifies scopes of the project. Provides internal review of the QAPP and approves the final QAPP.
Nancy Winters SCS, EAP Phone: 360-407-7392	Project Manager, Technical Lead, Primary Investigator	Writes the QAPP. Conducts field sampling and transportation of samples to the laboratory, with possible assistance of field crew. Conducts QA review of data, analyzes and interprets data. Writes the draft report and final report.
Kyle Graunke Field Staff –SCS, EAP	Field collection Coordinator	Assists in conducting field sampling, recording field data in field log book, and arranging and ensuring appropriate transportation of samples to the laboratory.
Allison Kingfisher W2R, Eastern Regional Office Phone: 509-329-3448	Building Materials Specialist	Facilitates RTF meetings, collaboratively develops agendas, communicates with RTF members, maintains list of members with phone numbers and email addresses.
Dale Norton SCS, EAP Phone: 360-407-6765	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Will Kendra SCS, EAP Phone: 360-407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Carol Kraege RTT, W2R Phone: 360-407-6906	Section Manager for Client	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Joel Bird MEL, EAP Phone: 360-871-8801	Director	Approves the final QAPP.
Tom Gries SCS, EAP Phone: 360-407-6327	NEP Quality Coordinator	Reviews draft QAPP and reports; recommends QAPP approval. May conduct field audit of project.
William R. Kammin EAP Phone: 360-407-6964	Ecology Quality Assurance Officer	Approves the draft QAPP and the final QAPP.

Table 3. Organization of project staff and responsibilities.

RTT: Reducing Toxic Threats Section

W2R: Waste 2 Resources Program

SCS: Statewide Coordination Section

EAP: Environmental Assessment Program

QAPP: Quality Assurance Project Plan

NEP: National Estuary Program

MEL: Manchester Environmental Laboratory

Field and laboratory work	Due date	Lead staff
Field work	Feb. to May 2013	Nancy Winters
Laboratory analyses completed	June 2013	MEL
Final report		
Author lead / Support staff	Nancy Winters	
Schedule		
Preliminary data presentation to RTF	August 2013	
Draft due to supervisor, client, NEP Quality Coordinator, and peer reviewers	September 2013	
Draft due to external reviewer(s)	November 2013	
Final (all reviews completed) due to publications coordinator	January 2014	
Final report due on web	February 2014	

Table 4. Proposed schedule for completing field and laboratory work, and reports.

Training

All 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 Manger their ability to properly set up the runoff collection bottles, operate the tipping bucket rain gage 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 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 procedures 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 conductivity), 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 conductivity 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 \pm 0.02 units. The MQO for the relative percent difference among the three replicate asphalt shingle panels is \pm 20 percent. EPA method 120.1 will be used to measure specific conductivity. 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 \pm 5 percent of the reading or 0.001 mS/cm, whichever is greater. The MQO for the relative percent difference for specific conductivity between the three replicate asphalt shingle panels is \pm 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 5 through 7), 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 5 through 7 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.

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.

Representativeness will be gauged by collecting and analyzing runoff from up to 10 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 0.1 and 0.75 inches of rain in a day and preceded by a 6-hour period with less than 0.1 inches).

For the leaching study, representativeness will be gauged by identifying coatings to be applied to the galvanized roofing materials that represent the types of after-market coating products available. For the copper roofing materials, the Copper Development Association will provide copper samples with and without two representative coatings.

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:

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

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 the sample and 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.

For the leaching study, replicate roof coupons with and without coatings will be subjected to the synthetic precipitation leaching procedure (SPLP). Precision for replicate samples results will be determined. The laboratory assesses its precision using the formula above 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. Synthetic precipitation blanks and method blanks will assist in determining for poor precision.

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 or amount of pollutant 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.

 $Accuracy = \frac{Measured value x 100}{True value}$

Tables 5 through 7 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 leaching study, synthetic precipitation blanks and method blanks will assist in determining bias and reasons for poor accuracy.

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 Ecology's standard operating procedures for field sampling (pH and conductivity analyses), decontamination procedures, and laboratory analyses in accordance with the *Manchester Environmental Laboratory Quality Assurance Manual* (MEL, 2012) 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 Clark et al. (2008) and Chang et al. (2004).

Completeness

Completeness is the comparison between the number of useable data points collected and the number identified in the plan. Completeness is measured as the percentage of total samples collected and analyzed as a whole and for individual parameters as compared to the goals established in this monitoring plan. Completeness will be measured as a percentage of usable samples of the total number of planned samples.

 $Completeness = \underline{No. \ planned \ samples} - \underline{No. \ of \ unacceptable/incomplete \ samples \ x \ 100}$ $No. \ planned \ samples$

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

The Ecology Manchester Environmental Laboratory (MEL) will meet all quality control (QC) requirements of the analytical methods being used for this project. Tables 5 through 7 list the MQOs for sensitivity, precision, accuracy, and completeness.

Analyte	Analysis / Prep. Methods	$\begin{array}{c} \text{MDL} \\ \left(\text{ug/L}\right)^1 \end{array}$	RL ² (ug/L)	Field Reps. & Splits (RPD)	LCS ³ (% R)	Matrix Spike (%R)	MS/ MSD ⁴ RPD	Completeness (%)
				Total Metals	5			
Arsenic	EPA 200.8	0.04	0.1	±20	85 - 115	75 - 125	±20	90%
Cadmium	EPA 200.8	0.0027	0.1	±20	85 - 115	75 - 125	±20	90%
Copper	EPA 200.8	0.033	0.1	±20	85 - 115	75 - 125	±20	90%
Lead	EPA 200.8	0.012	0.1	±20	85 - 115	75 - 125	±20	90%
Zinc	EPA 200.8	0.66	5	±20	85 - 115	75 - 125	±20	90%
			D	issolved Meta	als			
Arsenic	EPA 200.8	0.011	0.1	±20	85 - 115	75 - 125	±20	90%
Cadmium	EPA 200.8	0.0024	0.02	±20	85 - 115	75 - 125	±20	90%
Copper	EPA 200.8	0.0033	0.1	±20	85 - 115	75 - 125	±20	90%
Lead	EPA 200.8	0.0015	0.02	±20	85 - 115	75 - 125	±20	90%
Zinc	EPA 200.8	0.027	1	±20	85 - 115	75 - 125	±20	90%

Table 5. Measurement quality objectives for total recoverable and dissolved metals.

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

Analyte	Analysis / Prep. Methods	Method Detect. Limit (ug/L) ¹	Report Limit ² (ug/L)	Field Reps. & Splits (RPD)	LCS ³ (% R)	Matrix Spike (%R)	MS/ MSD ⁴ RPD	Completeness (%)
1-Methylnaphthalene	SW 8270D/ SW 3535A	NA ⁵	0.01	±40	50-150	50-150	±40	90%
2-Methylnaphthalene	SW 8270D/ SW 3535A	NA	0.01	±40	50-150	50-150	±40	90%
Acenaphthene	SW 8270D/ SW 3535A	0.0013	0.01	±40	40-112	55-97	±40	90%
Acenaphthylene	SW 8270D/ SW 3535A	0.0018	0.01	±40	10-126	48-103	±40	90%
Anthracene	SW 8270D/ SW 3535A	0.0023	0.01	±40	24-127	113-150	±40	90%
Benzo(a)anthracene	SW 8270D/ SW 3535A	0.0011	0.01	±40	38-147	59-137	±40	90%
Benzo(a)-pyrene	SW 8270D/ SW 3535A	0.0018	0.01	±40	14-129	42-110	±40	90%
Benzo(b)-fluoranthene	SW 8270D/ SW 3535A	0.0011	0.01	±40	42-133	53-99	±40	90%
Benzo-(g,h,i)-perylene	SW 8270D/ SW 3535A	0.0017	0.01	±40	12-122	38-131	±40	90%
Benzo(k)fluoranthene	SW 8270D/ SW 3535A	0.0012	0.01	±40	38-131	33-122	±40	90%
Chrysene	SW 8270D/ SW 3535A	0.0014	0.01	±40	37-128	51-116	±40	90%
Dibenzo(a,h)anthracene	SW 8270D/ SW 3535A	0.0015	0.01	±40	10-134	27-129	±40	90%
Dibenzofuran	SW 8270D/ SW 3535A	NA	0.01	±40	50-150	50-150	±40	90%
Fluoranthene	SW 8270D/ SW 3535A	0.0013	0.01	±40	42-123	60-107	±40	90%
Fluorene	SW 8270D/ SW 3535A	0.001	0.01	±40	50-150	50-150	±40	90%
Indeno(1,2,3cd) pyrene	SW 8270D/ SW 3535A	0.002	0.01	±40	29-129	37-135	±40	90%
Naphthalene	SW 8270D/ SW 3535A	0.0011	0.01	±40	41-105	41-97	±40	90%
Phenanthrene	SW 8270D/ SW 3535A	0.0024	0.01	±40	18-105	18-105	±40	90%
Pyrene	SW 8270D/ SW 3535A	0.002	0.01	±40	43-131	61-118	±40	90%

Table 6. Measurement quality objectives for PAHs.

Analyte	Analysis / Prep. Methods	MDL (ug/L) ¹	RL ² (ug/L)	Field Reps. & Splits (RPD)	LCS ³ (% R)	Matrix Spike (%R)	MS/ MSD ⁴ RPD	Completeness (%)	
	Phthalates								
Bis (2-Ethylhexyl) Phthalate	SW 8270D/ SW 3535A	0.093	0.2	±40	80-128	61-131	±40	90%	
Butylbenzylphthalate	SW 8270D/ SW 3535A	0.018	0.2	±40	23-183	80-150	±40	90%	
Diethylphthalate	SW 8270D/ SW 3535A	0.018	0.2	±40	77-123	79-117	±40	90%	
Dimethylphthalate	SW 8270D/ SW 3535A	0.013	0.2	±40	74-122	73-126	±40	90%	
Di-n-Butylphthalate	SW 8270D/ SW 3535A	NA	0.2	±40	70-156	73-148	±40	90%	
Di-N-Octylphthalate	SW 8270D/ SW 3535A	0.01	0.2	±40	75-135	61-148	±40	90%	
			PE	BDEs					
PBDE 47	SW 8270	0.000771	0.002	±40	50 - 150	50 - 150	±40	90%	
PBDE 49	SW 8270	0.000978	0.002	±40	50 - 150	50 - 150	±40	90%	
PBDE 66	SW 8270	0.00374	0.002	±40	50 - 150	50 - 150	±40	90%	
PBDE 71	SW 8270	0.000882	0.002	±40	50 - 150	50 - 150	±40	90%	
PBDE 99	SW 8270	0.001083	0.002	±40	50 - 150	50 - 150	±40	90%	
PBDE 100	SW 8270	0.001011	0.002	±40	50 - 150	50 - 150	±40	90%	
PBDE 138	SW 8270	0.002246	0.004	±40	50 - 150	50 - 150	±40	90%	
PBDE 153	SW 8270	0.00122	0.004	±40	50 - 150	50 - 150	±40	90%	
PBDE 154	SW 8270	0.00112	0.004	±40	50 - 150	50 - 150	±40	90%	
PBDE 183	SW 8270	0.001608	0.004	±40	50 - 150	50 - 150	±40	90%	
PBDE 184	SW 8270	0.001144	0.004	±40	50 - 150	50 - 150	±40	90%	
PBDE 191	SW 8270	0.00147	0.004	±40	50 - 150	50 - 150	±40	90%	
PBDE 209	SW 8270	0.003262	0.01	±40	50 - 150	50 - 150	±40	90%	

Table 7. Measurement quality objectives for phthalates and PBDEs.

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 yet available from MEL

Study Design

Roofing Types and Products

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 2. Roofing material types were selected based on three criteria:

- 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 8 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 in comments to the draft QAPP.

Roof Type	Percent of Puget Sound Basin			
51	Surface Area			
Asphalt Shingle	71%			
Built-up	13			
Wood Shingle	6.5			
Metal	5.3			
Concrete tile	2.9			
Copper	<1			
Clay Tile	<1			
Masonite	<1			
Other	<1			

Table 8. Percent of roof surface area in the Puget Sound basin represented by each roof type.

Manufacturers and associations met to determine the products they believed best represented the market in the Pacific Northwest and that they were willing to donate. To ensure that the specific manufacturer-selected roofing materials were within the range of products available for a roofing type, X-ray fluorescence (XRF) analyses will be conducted.

Manufacturers will be requested to submit a wide variety of samples ("coupons") of their materials for XRF analysis. The Thermo Fisher Scientific Niton XRF Analyzer uses radiation to determine the metal and bromine composition of a sample. The penetration of the x-rays depends on the density of the material between 0.05 and 2 millimeters. Bromine is an indicator of the presence of brominated flame retardants. The results of these analyses will be compared to a field XRF analysis once the panels have been installed to determine whether metals and bromine concentrations of the installed panels are within the ranges of the supplied coupons.

Source: Appendix B of Ecology 2011a.

Pilot-Scale Roofing Panels

Ecology staff and manufacturers' representatives will construct 18 roofing pilot panel assemblages (testing 14 specific roofing material types, triplicate panels of the asphalt shingle without algae-resistant, copper-containing granules, 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. The glass controls will be used to subtract out the pollutant contribution from wet and dry deposition. Ecology will construct 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), and because the data will be comparable to the studies by Clark (2010) and Chang et al. (2004). The low slope roof types and one control will be sloped at 1.2° (1/4:12 slope) (ARMA, 2012). Using industry-standard slopes for the pilot panel types allows comparison to data collected from actual installed roofs. Figure 2 depicts the pilot-scale panel design used by Clark et al. (2008) and mimicked in this study.

Ecology staff will construct a frame for each 4 ft. by 8 ft. panel. The panels, except for glass (controls), will be provided by the manufacturers. The manufacturers or their representatives will install the panels on site. Manufacturers who provide panels will be asked to construct the panels as they would be constructed on an actual roof, to the extent feasible. Manufacturers and/or associations will submit suggested installation detail for review by Ecology to ensure results will not be biased by the installation. Manufacturers/associations are encouraged to install their roofing panels with nails, fasteners, adhesives or other seaming materials in proportion to those found on a constructed roof. Panels will not include flashing materials, gutters and downspouts, or any HVAC systems.

Ecology will place the pilot-scale roofing panels and associated sampling equipment in a secure area at the Ecology Headquarters facility in Lacey, Washington for exposure to local rain conditions. All will face south-southwest at 206° of true north, the direction of the prevailing wind direction (OWSC, 2012). Panel assemblages will be leveled. This location will ensure that all panels are exposed to the same precipitation event and the same wind direction simultaneously.

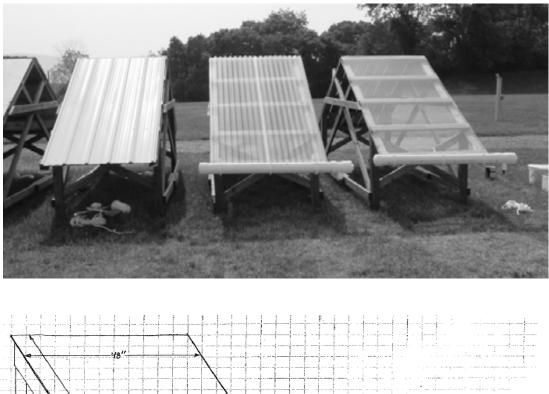
Ecology will randomize the panel order within linear arrangements (low slope in one row, high slope in a second row) using Minitab[®]. The triplicate asphalt shingle panels will be placed in a third row.

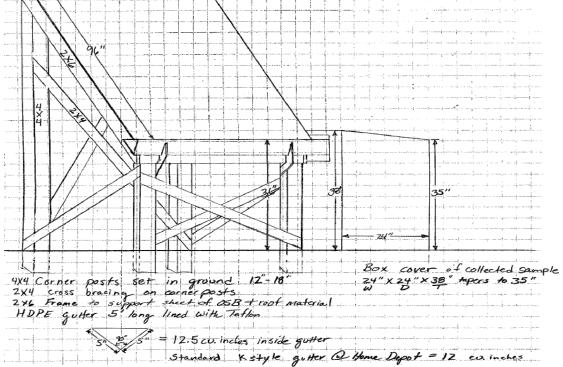
Panels will be placed at least 100 feet from trees or other potential obstructions to precipitation. They will be a minimum of 3 feet from the ground surface at the lower edges and on 10-foot centers from one another to prevent splash from the ground or adjacent panels. Panels will be at least 10 feet from the security fence.

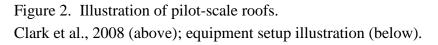
Panels will be secured with a locked security fence. Ecology's security crew will check on the panels at least two times per shift.

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.

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.







Ecology will collect samples from rain events generating at least 7.5 liters (minimum required for analyses) but not more than 56 liters (container maximum). The samples represent 100% of a rainfall event and will provide the equivalent of an event mean concentration. Ecology will deploy a tipping bucket rain gage 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

Ecology will install a tipping bucket rain gage onsite at the Ecology facility in Lacey, Washington to monitor rain depth and intensity. The rain gage tips and records at least every 0.01 inch of precipitation. The rain gage 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 Olympia area on at least a daily basis from:

- National Weather Service Forecast Office operated by the National Oceanic and Atmospheric Administration (NOAA) <u>www.wrh.noaa.gov/sew</u>
- AccuWeather at <u>www.accuweather.com/en/us/united-states-weather</u>
- KOMO news at <u>www.komonews.com/weather</u>

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. 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. This represents the 40.5 percentile of the daily rainfall depths for this location, based on a period of record from January 1, 1955 through December 31, 2011 (Howie and Labib, pers. comm., 2012). 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, or the 90.8 percentile of the daily rainfall events for this area based on the same period of record. Rain events will not exceed 24 hours.

The minimum antecedent dry period between rain events is defined as 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 Ecology to capture the appropriate runoff volumes for analysis, while allowing for low intensity or long duration events.

Ecology will collect and analyze runoff samples from a maximum of 10 rain events between 0.1 and 0.75 inches between February and May 2012.

Analyses

Runoff samples from all roof types will be analyzed for total recoverable (total) metals for five metals (arsenic, cadmium, copper, lead and zinc). Four of 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). Lead has also been identified as a contaminant of concern in the literature (Table A-1 Appendix A). During three precipitation events that provide at least 8 liters of runoff, runoff from all panels will be analyzed for both total and dissolved metals to verify the literature assertion that vast majority of the metals in roof runoff exist in the dissolved phase.

Runoff from all panels and from the first three rain events will also be analyzed for PAHs, phthalates and PBDEs. Thereafter, only runoff from the asphalt shingle, BUR, and single-ply roofs (TPO, PVC, and EPDM) will be analyzed for PAHs and phthalates. Evidence of PAHs and phthalates in runoff from roofing materials has been documented in the literature (Appendix A), although it is uncertain whether all of these chemicals originate in the roofing materials or from atmospheric deposition. Additionally the Draft PAH Chemical Action Plan (Ecology 2012b) identified roofing as a potential source of PAHs that needed to be evaluated.

Single-ply roofing materials will also be analyzed for PBDEs (flame retardants) that may be an added component of some roofing materials, as needed to meet fire codes. Table 9 lists parameters that will be analyzed by roofing types for the first three rain events and Table 10 lists the parameters that will be analyzed for the remaining rain events. Estimated analytical costs are provided in Appendix D.

Roof Type	Total Metals ^a	PAHs + Phthalates	PBDEs		
Steep Slope					
Asphalt shingle - composite 6 types of shingles without copper-containing granules for algae control	3	3	3		
Asphalt shingle - composite 6 types of shingles with copper-containing granules for algae control	1	1	1		
Copper	1	1	1		
Manufacturer-painted galvanized steel	1	1	1		
Concrete tile	1	1	1		
Wood shingle/shake	1	1	1		
Manufacturer-treated wood shingle/shake	1	1	1		
Low Slope					
Thermoplastic polyolefin (TPO)	1	1	1		
Polyvinyl chloride (PVC)	1	1	1		
Ethylene propylene diene monomer (EPDM)	1	1	1		
Zincalume®	1	1	1		
Built-up roof (BUR) with oxidized asphalt granulated cap sheet	1	1	1		
Modified BUR with SBS granulated cap sheet	1	1	1		
Modified BUR with APP granulated cap sheet	1	1	1		
Controls					
Steep slope glass control	1	1	1		
Low slope glass control	1	1	1		

Table 9. Analyses by roofing type for each of the first three rain events (number of samples per event shown).

^a Dissolved metals will be analyzed for all panels up to three events for the entire study, if the event produces 8 liters or more of runoff

Roof Type	Total Metals ^a	PAHs + Phthalates	PBDEs		
Steep Slope					
Asphalt shingle - composite 6 types of shingles without copper granules for algae control	3	3			
Asphalt shingle - composite 6 types of shingles with copper granules for algae control	1	1			
Copper	1				
Manufacturer-painted galvanized steel	1				
Concrete tile	1				
Wood shingle/shake	1				
Manufacturer-treated wood shingle/shake	1				
Low Slope					
Thermoplastic polyolefin (TPO)	1	1	1		
Polyvinyl chloride (PVC)	1	1	1		
Ethylene propylene diene monomer (EPDM)	1	1	1		
Zincalume®	1				
Built-up roof (BUR) with oxidized asphalt granulated cap sheet	1	1			
Modified BUR with SBS granulated cap sheet	1	1			
Modified BUR with APP granulated cap sheet	1	1			
Controls					
Steep slope glass control	1	1	1		
Low slope glass control	1	1	1		

Table 10. Analyses by roofing type for each of the remaining rain events (number of samples per event shown).

^a Dissolved metals will be analyzed for all panels up to three events for the entire study, if the event produces 8 liters or more of runoff

Leaching Procedure

As resources allow and in coordination with laboratory availability, metal roofing samples ("coupons") will be exposed to a laboratory leaching procedure to assess the relative leaching with and without post-manufactured coatings. The timing of these analyses is independent of the evaluation of the pilot panels. Small replicate samples of metal roofing material with and without coatings will be exposed to a modified Synthetic Precipitation Leaching Procedure (SPLP) (EPA Method 1312). These analyses will be used to determine whether post-manufactured coatings can reduce the leaching of metals from roofing materials without contributing other contaminants to the leachate.

A sub-group of the RTF will recommend up to six sealants/treatments for galvanized steel roofs and three for a copper roof that are representative of the market. Snow Seal® will be evaluated as one of the coatings for galvanized roofs because this product is being recommended for use to reduce zinc in runoff from galvanized steel roofs for Industrial Stormwater General permittees (Killelea, pers. comm. 2012). Coupons will be standardized to 1 inch squares. Both sides of each coupon will be exposed (either coated or not coated). Edges of the roofing material will also be coated.

The SPLP method was designed to assess the potential for contaminants to leach in a simulated rain medium during the 18- to 20-hour exposure. According to Taylor Associates (2004) the SPLP leachate is slightly more aggressive than rain in the Puget Sound region because it has a slightly lower pH and lower ionic strength than rain. The modifications to the SPLP method are described in Appendix E and designed to assess the concentration in the leachate per surface area, rather than by weight. The modification is also designed so that the synthetic rain to surface area simulates the volume of precipitation received per square inch of surface area in one year in Olympia, Washington.

Leachate will be analyzed for five metals, PAHs and phthalates using the methods and measurement quality objectives described in Tables 5 through 7. Table 11 provides a list of the analyses to be conducted for each sample. These analyses will be used for approximation of the percent reduction achieved by the coatings. Three replicates will be prepared for each coupon. SPLP blanks and matrix spike/matrix spike duplicates (MS/MSDs) will be analyzed at a rate of one set per batch of 20 samples.

If discussions with coatings manufacturers reveal that coatings constituents include other contaminants of concern, the list of analytes will be amended to include those parameters. Appendix D provides estimated laboratory costs for this portion of the project.

Data from this portion of the project will be assessed to determine (1) the percent reduction of metals with specific coatings on a unit area basis, and (2) whether the coatings leach other constituents of concern to the simulated precipitation.

Coupon Type	Total Metals (As, Cd, Cu, Pb, Zn) EPA 200.8	PAHs + Phthalates EPA 8270D	
Galvanized steel	3	3	
Zincalume®	3	3	
Galvanized steel with sealant 1 (Snow Seal*)	3	3	
Galvanized steel with sealant 2	3	3	
Galvanized steel with sealant 3	3	3	
Galvanized steel with sealant 4	3	3	
Galvanized steel with sealant 5	3	3	
Galvanized steel with sealant 6	3	3	
Copper	3	3	
Copper with sealant 1	3	3	
Copper with sealant 2	3	3	
Copper with sealant 3	3	3	
SPLP blank	4	4	
MS/MSD	8	8	
Total for SPLP extractions	48	48	

Table 11	Replicates of roofing	coupons for anal	yses of SPLP leachate.
	Replicates of footing	coupons for anal	yses of SFLF leachate.

*Based on Ecology Water Quality Program's recommendation for use of Snow Seal in reducing zinc from roof runoff at facilities under the Industrial Stormwater General Permit.

Sampling Procedures

Following construction and roofing panel installation on site, each panel, panels will be covered with plastic sheeting until they are all decontaminated on the same day. Field staff will decontaminate all roofing panels, gutters, and sample collection equipment using the procedures described in Appendix C. Representative pictures will be taken for presentation in the report.

Field staff will deploy a tipping bucket rain gage and data logger at the Ecology headquarters facility in Lacey, Washington. The rain gage 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 full 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 C. Equipment rinse samples will be obtained to ensure all equipment is contaminant-free (see Quality Control Procedures).

Following 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 gage 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 MEL precleaned sample bottles with a peristaltic pump and Teflon® tubing as described in Appendix C. Samples for dissolved metals will be field-filtered and will be poured into pre-preserved sample bottles. Field splits MS, and MSD samples of runoff will be taken from three of the roofing panels for which replicate panels do not exist. 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 conductivity of the remaining contents of the stainless-steel container as described in Appendix C and following Ecology standard operating procedures EAP031 and EAP032 (Ward 2006 and 2011, respectively).

The laboratory staff will add preservative to the total and dissolved metals sample bottles. Table 12 describes the appropriate sample containers, required sample volumes, sample containers, preservation methods, and holding times.

Field staff will apply the pre-prepared (laboratory tags) to each sample bottle, 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 MEL within 2 days of collection as described in Appendix C. An example chain of custody form specific to this project is provided in Appendix C.

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 C. Distilled deionized water from the laboratory will be used of all the post-decontamination equipment rinse samples. A sample of the laboratory distilled 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 C, and will download data from the rain gage data logger.

Parameter	Method	Sample Matrix	Sample Size	Bottles	Preservation	Holding time
Total metals (As, Cd, Cu, Pb, Zn)	EPA 200.8	water	500 mL	500 mL HDPE	HNO₃ to pH<2 Cool to <u>≤</u> 6°C	6 months
Dissolved metals (As, Cd, Cu, Pb, Zn)	EPA 200.8	water	500 mL	500 mL HDPE	Field filter, and HNO ₃ to pH<2 Cool to ≤6°C	15 min. to preservation; 6 months
PAHs and phthalate (collected in the same bottle)	EPA 8270D	water	1 L	1 L amber glass	HCl to pH<2, Cool to ≤6°C	7 days to extraction/ 14 days after extraction
PBDEs	EPA 8270D	water	1 L	1 L amber glass	Cool to $\leq 6^{\circ}$ C	7 days to extraction

Table 12. Sample bottles, preservation, and holding times.

Measurement Procedures

Table 13 lists the analyses to be performed and the number of samples anticipated for each rain event. Estimated costs for analyses are provided in Appendix D. The project manager will notify MEL staff when precipitation of ample volume is anticipated and will confirm just before samples are processed to notify the laboratory of anticipated schedule of delivery. Because Ecology will conduct the evaluation at the Ecology facility, the schedule will depend on specific rainfall events. The available literature describes the range of anticipated metals concentrations as presented in Table A-1 Appendix A.

Tables 5, 6, and 7 list the reporting limits, and method detection limits. MEL 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).

Sample	Total Metals	Dissolved Metals*	PAHs & Phthalates	PBDEs						
First Three Sampling Events										
Panels 18 up to 18 18 18										
QA and Other Samples	•									
Field splits	3	up to 3	3	3						
MS/MSD	6	up to 6	6	6						
Filter blank	0	up to 2	0	0						
Distilled deionized water blank	1	0	1	1						
Equipment rinse blank	1	up to 1	1	1						
Total Samples/Event for first three rain events	29	30	29	29						
F	Remaining Sam	pling Events								
Panels	18	up to 18	12	5						
QA and Other Samples										
Field splits	3	up to 3	3	1						
MS/MSD	6	up to 6	6	2						
Filter blank	0	up to 2	0	0						
Distilled deionized water blank	1	0	1	1						
Equipment rinse blank	1	up to 1	1	1						
Total Samples/Event for remaining events	29	30	23	10						

Table 13. Numbers of samples by analysis per rain event for first three and remaining sampling events of the pilot-scale roof runoff study.

*Dissolved metals will be analyzed for all panels up to three events for the entire study, if the event produces 8 liters or more of runoff.

Quality Control Procedures

Field Quality Control

Two parameters will be analyzed in the field for the pilot-scale roof study, pH, and specific conductivity, following SOPs EAP031 and EAP032, respectively (Ward 2006 and 2011). 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 conductivity 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 C 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. Field splits and runoff water for MS/MSDs will be collected as shown in Table 14 at a rate of 20% 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 5 through 7. 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 C).

Prior to installing the panels, field staff will collect final distilled water rinses from at least three of the cleaned gutters to ensure proper cleaning. 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 the laboratory provide distilled water blanks to determine whether the distilled water contains any of the contaminants of concern.

Laboratory Quality Control

The laboratory quality control procedures routinely followed by MEL will satisfy the purposes of this project. MEL will follow standard operating procedures as described in the *Manchester Environmental Laboratory Quality Assurance Manual* (MEL, 2012) and the *MEL Laboratory Users Manual* (MEL, 2008). Table 14 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 20% of the 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, phthalates, and PBDEs. The laboratory duplicate 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 5 though 7.

Parameter (Method)	LCS ^a	Method Blank	Field Split / Analytical Duplicate	MS/MSD
Total metals (As, Cd, Cu, Pb, Zn)	1/batch ^b	1/batch	20% of samples or 1/rain event, whichever is greater	20% of samples or 1/rain event
Dissolved metals (As, Cd, Cu, Pb, Zn)	1/batch	1/batch	20% of samples or 1/rain event, whichever is greater for three rain events	20% of samples or 1/rain event for three rain events
PAHs & phthalates	1/batch	1/batch	20% of samples or 1/rain event, whichever is greater	20% of samples or 1/rain event
PBDEs	1/batch	1/batch	20% of samples or 1/rain event, whichever is greater	20% of samples or 1/rain event

Table 14. Laboratory quality control samples for pilot-scale roof runoff study.

^a LCS: Laboratory control sample

^b One batch consists of 20 samples of less

For the SPLP leaching study, laboratory quality control procedures routinely followed by MEL will satisfy the purposes of this project. MEL will follow standard operating procedures as described in the *Manchester Environmental Laboratory Quality Assurance Manual* (MEL, 2012) and the *MEL Laboratory Users Manual* (MEL, 2008).

MS/MSD samples will be analyzed at a rate of one per batch (5% of the samples). An SPLP blank will also be conducted at a rate of one per batch. The laboratory will analyze the quality control samples for metals, PAHs, and phthalates as described in Table 15.

Parameter (Method)	LCS ^a	Method Blank	SPLP Blank	MS/MSD
Total metals (As, Cd, Cu, Pb, Zn)	1/batch ^b	1/batch	1/batch	1/batch
PAHs & phthalates	1/batch	1/batch	1/batch	1/batch

^a LCS: Laboratory control sample

^b One batch consists of 20 samples of 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 Ecology's Z drive (backed up nightly). The project manager or designee will tabulate data and information from the chain of custody form and the field notebook (Appendix C). MEL 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 Ecology's Z drive until it is incorporated into the report.

Data Verification and Validation

Ecology staff will examine data for errors or omissions and compliance with QC acceptance criteria. Field staff will check field notebooks for missing or improbable measurements at the end of a sampling event. Field staff will review field notes, correct missing data, and highlight unusual data for subsequent project manager consideration. Field staff 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 MEL *Laboratory Users Manual* (MEL, 2008). 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 *Lab Users Manual*. MEL 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 5 through 7.
- Laboratory control samples and method blanks that do not meet the precision and accuracy goals in Tables 5 through 7.

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

The project manager will check data received from MEL for omissions against the Request for Analysis forms. The project manager will review the data for reasonableness and consistency and will confirm that the data meet the measurement quality objectives of the project. The project manager 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 project manager 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 project manager 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 project manager 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 project manager 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 project manager envisions the following analyses in either tabular or graphical format, depending on the usability of the data.

Pilot Roofing Study

- Evaluation of median and ranges for each roofing panel over the timeframe of the study.
- Assessment of the aerial deposition (wet and dry) on the two control panels.
- Assessment of contaminant concentrations (minus the aerial deposition) for each panel type over the length of the study.
- Comparisons of medians and ranges of contaminant concentrations (minus the aerial deposition) between roofing types.
- Calculation of contaminant releases on a mass basis per unit area (ug/m2) and on a mass per area rain depth (ug/m2 /mm).

- Assessments of potential impact of rain intensity on contaminant concentrations within roofing types, if an adequate range of intensities is available.
- Comparison of the three replicate asphalt shingle panels without AR.

SPLP Leaching Study

- Determination of medians and ranges of contaminant concentrations in the SPLP leachate by coating type.
- Comparisons by coating type of percent reductions in contaminants released.
- Assessment of whether other contaminants were released from the coatings.

Results of the most relevant comparisons and analyses will be presented in the report in tabular and graphical format. The project manager will draw conclusions from the analyses of the results, will use best professional judgment to assess the adequacy of the study design, and will propose potential solutions for any deficiencies for future studies.

Audits and Reports

Audits

MEL participates in performance and system audits of their routine procedures. Audits may be conducted by the NEP QC Coordinator. The public may request results of these audits in writing.

Data Reporting

The project manager will prepare a draft and final report in accordance with the schedule in Table 3. The report will include the following:

- Description of field and laboratory methods.
- Deviations from this QAPP.
- Photographs of the roofing panel setup.
- Comparison of the ranges of the XRF analyses from the samples provided by the manufacturers to those used for the installed panels for the five metals of concern and bromine.
- 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.
- Presentation of roof runoff quality from the roofing materials tested on a concentration (ug/L), mass basis per unit area (ug/m2), and mass per area rain depth (ug/m2 /mm).
- Comparisons of medians and ranges of contaminant concentrations and loadings (minus the aerial deposition) between roofing types.
- Comparisons of study data with literature values.
- Comparisons of percent reductions achieved by coatings and discussion of whether other contaminants of concern were detected in the leachate.
- 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.

Ecology reviewers, including the NEP QC Coordinator, will comment on a draft of the report. These comments will be addressed before the RTF members receive a copy of the draft report for their review and comment. The project manager will address comments and prepare the final investigative report by February 2014. Ecology will provide public access to electronic versions of the report generated from this project via Ecology's internet homepage (www.ecy.wa.gov). The data generated will be stored in EXCEL files and be available upon request at the end of the project.

The data generated from this study will be used to assess regionally-used roofing materials as potential sources of contaminants in the Puget Sound basin. It is anticipated that Ecology will work with participants in the RTF to assess the data collected and make recommendations for follow-up actions and additional studies that may need to be conducted. Recommendations for ways to reduce contaminant releases from roofing materials will also be considered in conjunction with the RTF.

References

ARMA. 2012. Letter from John Ferraro, Asphalt Roofing Manufacturers Association, to Nancy Winters, Department of Ecology concerning Comments on Quality Assurance Project Plan – Roofing Materials Assessment – Investigation of Toxic Chemicals in Roof Runoff. December 21, 2012.

Bannerman, R., K. Baun, M. Bohn, P. Hughes, and D.A. Graczyk. 1983. Evaluation of Urban nonpoint source pollution management in Milwaukee County Wisconsin. U.S. Environmental Protection Agency Publication No 84-114164.

Boller, M. 1997. Tracking heavy metals reveals sustainability deficits of urban drainage systems. Water Science & Technology. 35(9):77-87.

Chang, M., M. McBroom, and R. Beasley. 2004. Roofing as a source of nonpoint pollution. Journal of Environmental Management 72: 307-315.

Clark, S.E., K.A. Steele, J. Spicher, C.Y.S. Siu, M.M. Lalor, R. Pitt, and J.T. Kirby, J.T. 2008. Roofing materials' contributions to storm-water runoff pollution. Journal of Irrigation and Drainage Engineering. 34(5), 638-645.

Ecology. 2012a. Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies. Washington State Department of Ecology, Environmental Assessment Program. Olympia, WA. October, 2012. https://fortress.wa.gov/ecy/publications/SummaryPages/0403030.html

https://fortress.wa.gov/ecy/publications/SummaryFages/0405050.html

Ecology. 2012b. Draft PAH Chemical Action Plan (CAP). Washington State Department of Ecology, Olympia, WA. Publication No. 12-07-038. July 2012. https://fortress.wa.gov/ecy/publications/publications/1207038.pdf

Ecology. 2011a. Control of Toxic Chemicals in Puget Sound Phase 3: Primary Sources of Selected Toxic Chemicals and Quantities Released in the Puget Sound Basin. Washington State Department of Ecology, Olympia, WA. Publication No. 11-03-024. https://fortress.wa.gov/ecy/publications/summarypages/1103024.html

Ecology. 2011b. Control of Toxic Chemicals in Puget Sound: Assessment of Toxic Chemical Loads in the Puget Sound Basin, 2007-2011. Washington State Department of Ecology, Olympia, WA. Publication No. 11-03-055. https://fortress.wa.gov/ecy/publications/summarypages/1103055.html

Ecology. 2011c. Technical Guidance Manual for Evaluating Emerging Stormwater Treatment Technologies, Technology Assessment Protocol – Ecology (TAPE). Washington State Department of Ecology, Olympia, WA. Publication No. 11-10-061. <u>https://fortress.wa.gov/ecy/publications/publications/1110061.pdf</u> Good, J. 1993. Roof runoff as a diffuse source of metals and aquatic toxicity in stormwater. Water Science Technology 28 (3-5): 317-321.

Gromaire, M.C., P. Robert-Sainte, A. Bressy, B. Gouvello, and G. Chebbo. 2010. Zn and Pb emissions from roofing materials – Modeling and mass balance attempt at the scale of a small urban catchment. NOVATECH 2010, Session 2.9.

Howie, D. and F. Labib. 2012. Personal communication between Doug Howie, Foroozan Labib, and Nancy Winters, Washington State Department of Ecology, concerning use of the Western Washington Hydrology Model (WWHM) 2012 to determine rain intensities and depths from historic data. November 2, 2012.

Khan, B.I., H.M. Solo-Gabriele, T.G. Townsend, and Y. Cai. 2006. Release of arsenic to the environment from CCA-treated wood. 1. Leaching and speciation during service. Environmental Science and Technology. 40(3): 988-993.

Killelea, J. 2012. Personal communication between Jeff Killelea and Nancy Winters, Washington State Department of Ecology. October 15, 2012.

Malarkey, G. 2012. Discussion of typical roofing processes and practices between Greg Malarkey, Malarkey Roofing Products, and Nancy Winters, Department of Ecology, Environmental Assessment Program. October 26, 2012.

MEL. 2008. Manchester Environmental Laboratory Lab Users Manual, Ninth Edition. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

MEL. 2012. Manchester Environmental Laboratory Quality Assurance Manual. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

NADP. 2012. National Atmospheric Deposition Program. Chemical data from 2000 through 2010 accessed for the following five stations: Olympic National Park – Hoh Ranger Station, Mount Rainier National Park – Tahoma Woods, North Cascades National Park – Marblemont Ranger Station, Le Grande, and Columbia River Gorge. Website accessed July 10, 2012 : http://nadp.sws.uiuc.edu/sites/sitemap.asp?state=wa

OWSC. 2012. Office of Washington State Climatologist. Website accessed July, 2012: www.climate.washington.edu/windrose/Olympia-WindRose.pdf

Paulson, A.J., B. Carter, and R. Shiebley. 2011 (Draft). Control of Toxic Chemicals in Puget Sound: Assessment of Toxic Chemicals in the Puget Sound Basin Addendum No. 1 – Evaluation of Fate and Transport Mechanisms for Primary Releases of Copper, Polychlorinated Biphenyls, and Polybrominated Diphenyl Ethers in the Puget Sound Basin.

Pitt, R. and M. Lalor. 2000. Module 4d: The role of pollution prevention in stormwater management. Presented at the 2000 Conference on stormwater and Urban Water Systems Modeling. Toronto, Canada. February 24-25.

Pitt, R. Pitt, R., M. Lilburn, S. Nix, S.R. Durrans, S. Burian, J. Voorhees, and J. Martinson. 2000. Guidance Manual for Integrated Wet Weather Flow (WWF) Collection and Treatment Systems for Newly Urbanized Areas (New WWF Systems). U.S. Environmental Protection Agency. 612 pgs.

Puget Sound Estuary Program (PSEP). 1997. Recommended Guidelines for Measuring Organic Compounds in Puget Sound Water, Sediment, and Tissue Samples. Final Report. Prepared for U.S. Environmental Protection Agency, Seattle, WA.

Steuer, J., W. Selbig, N. Hornewer, and J. Prey. 1997. Sources of Contamination in an Urban Basin in Marquette, Michigan and an Analysis of Concentrations, Loads, and data Quality. United States geological Survey, Water-resources Investigations Report 97-4242. 25 pages.

Taylor Associates, Inc. 2004. Zinc leaching study: an assessment of zinc sources to stormwater runoff. Prepared for Port of Seattle, Seattle-Tacoma International Airport. Prepared by Taylor Associates, Inc, Seattle, WA. February 2004.

Walat, J. 2012. Discussion and meeting about EPA Urban Waters grant to study roofing runoff in the Puget Sound region. Jean Walat, Port Townsend Marine Science Center, and Nancy Winters, Department of Ecology, Environmental Assessment Program. August 9, 2012.

Ward, W.J. 2011. Standard Operating Procedures for the Collection and Analysis of Conductivity Samples, Version 2.1. Washington State Department of Ecology, Olympia, WA. SOP Number EAP032. <u>www.ecy.wa.gov/programs/eap/quality.html</u>

Ward, W.J. 2010. Standard Operating Procedure for the Collection and Field Processing of Metals Samples, Version 1.4. Washington State Department of Ecology, Olympia, WA. SOP Number EAP029. www.ecy.wa.gov/programs/eap/quality.html

Ward, W.J. 2006. Standard Operating Procedures for the Collection and Analysis of pH Samples, Version 1.3. Washington State Department of Ecology, Olympia, WA. SOP Number EAP031. www.ecy.wa.gov/programs/eap/quality.html

Yaziz, M.I., H. Gunting, N. Sapari, and A.W. Ghazali. 1989. Variations in rainwater quality from roof catchments. Water Research 23 (6):761-765.

Appendices

Appendix A. Literature Review

A previous study by the Washington State Department of Ecology (Ecology) indicated that roofing materials appear to be major sources of copper, cadmium, zinc, arsenic, and possibly PAHs and phthalates in the Puget Sound basin (Ecology, 2011a and b). However, the assessment used literature values from various locations across the U.S. and the world to represent contaminant concentrations. A number of regional factors such as precipitation, pH, and materials used could have a significant impact on the release of contaminants from roofing materials.

Ecology has received funding from the National Estuary Program (NEP) to conduct an assessment of roofing materials in the Puget Sound basin. This study will evaluate the runoff from constructed 4 by 8 foot pilot-scale roof panels exposed to precipitation in Olympia, Washington. The literature review provides background information considered during the development of the study.

This literature review includes information organized in the following sections:

- Introduction
- Puget Sound Basin Roofing Assessment
- Metal roofs
- Non-metal Roofs
- Vegetative Roofs
- Other Factors Affecting Contaminants in Roof Runoff
- Aerial Deposition.

Introduction

Researchers have studied the contribution of contaminants from roof runoff to stormwater for over two decades. In a comprehensive analysis of the constituents in stormwater, Eriksson (2002) reported that 78 metals and other inorganics and 385 anthropogenic organics have been found in urban stormwater runoff. While not all of these are associated with runoff from roof tops, the list is extensive. Construction materials including roofing materials have the potential to release arsenic, cadmium, chromium, copper, lead, nickel, and zinc, phthalates, biocides, nonyl phenols, and thiocyanate (Bjorklund, 2011). The contaminants emanating from roof tops likely discharge to rivers, streams, and other waterbodies and may adversely affect aquatic life. Stormwater research associated with roofing materials has focused predominantly on the contribution of heavy metals (Bannerman et al., 1983; Boller, 1997; Steuer et al., 1997; Good, 1993; Yaziz et al., 1989; Quek and Förster, 1993; Davis et al., 2001; Pitt and Lalor, 2000; and Lye, 2009). These metals have been reported to contribute up to 80% of the cadmium, lead, and zinc to wet weather flows of Paris (Gromaire et al., 2001).

A recent assessment of the anthropogenic sources and annual releases of toxic chemicals to the Puget Sound basin identified roof runoff to be a significant contributor of certain metals and comparatively minor sources of phthalates and polycyclic aromatic hydrocarbons (PAHs) (Ecology, 2011a). Ecology obtained information on chemical concentrations used to derive

these estimates primarily from the published literature. Table A-1 summarizes the concentration ranges used for the loading study. The study found that approximately 80% of the zinc, 60% of the cadmium, 20% of the arsenic, and 10% of the copper released in the Basin were associated with roof runoff (Ecology 2011a).

Chemical	Estimated Range of Concentrations (ug/l)	Estimated Annual Release in the Puget Sound Basin (t/yr)	Contribution to Total Anthropogenic Release
Arsenic	-<0.01 - 1.43	< 0.01 - 0.84	19%
Cadmium	0.24 - 1.9	0.5 - 0.7	53 - 68%
Copper	4 - 1,850	12 - 43	3% - 29%
Lead	< 0.1 - 52	15 - 20	2% - 12%
Zinc	24.6 - 16,317	210 - 2,800	37% - 97%
PAHs	0.61 - 2.06	0.6	0.02%
Bis (2-ethylhexyl) phthalate	a	0.14	<1%

m 11 4 4		0 1 1		c	o i i	D	a 11 1
Table A-1	Estimated release	of selected	chemicals	from roo	nting in t	ne Piliget (Sound basin
140101111	Lotiniated release	or beleeted	cifetitieuto	110111100	ing in a	ne i uget i	Sound busin.

Source: Ecology, 2011a

^a Annual release estimate based on amount of PVC and non-polymers used in Washington (Ecology 2011a)

Puget Sound Basin Roofing Assessment

A comprehensive and controlled assessment of runoff from various roofing materials has not been conducted under the unique climatic conditions of Western Washington. Low-intensity, long-duration rainfalls dominate from October until May or June each year. While Western Washington experiences acidic rain ranging in pH from 4.95 to 5.4 (NADP, 2012), these pH values are substantially higher than the pH values measured by Clark in the most extensive studies controlled for atmospheric deposition of roofing materials in the U.S. (Clark, 2010). Her studies were conducted in central Pennsylvania where the pH of the rain was approximately 4.3.

Further, little evaluation has been conducted of the newer, synthetic materials such as ethylene propylene diene monomer (EPDM or rubber roofing), thermoplastic polyolefin (TPO), and flexible PVC. These types of roofs may also be expected to release phthalates into roof runoff. Nor have researchers evaluated PAHs in runoff from built-up roofs (BUR) installed using either coal tar or asphalt, or asphalt shingle roofs. Modified BURs can include asphalt layered with a substrate such as Atactic Polypropylene (APP) or Styrene Butadiene Styrene (SBS). Runoff from these materials has not been assessed for many of the chemicals that could potentially leach from them.

Most studies have been conducted in the field and may or may not have accounted for aerial deposition. A controlled, outdoor study could provide controls for precipitation intensities, durations, and depths experienced in the Puget Sound region. A study conducted in the Puget Sound region that controls for aerial deposition would provide an understanding of the contaminants and concentrations emanating from the roofing materials rather than from atmospheric deposition.

Metal Roofs

Metal roofs are often constructed from thin sheets of either zinc, copper, or galvanized zinc. Galvanization produces a thin layer of zinc to cover another metal and prevent its corrosion. All metal roofs are susceptible to oxidization and corrosion releasing metals in both particulate and water soluble forms. Elevated concentrations of copper and zinc have been reported in runoff from roofs, gutters, and downspouts composed of these materials. Total copper concentrations in runoff from older and newer roofs ranged from 1,000 to 1,967 ug/L, respectively (Pennington and Webster-Brown, 2008). Barron (2000) measured concentrations of copper in steady-state flows (i.e., following first flush effects) between 900 and 2,000 ug/L, while first flush flow concentrations were substantially higher. Karlén et al. (2002) reported runoff from copper roofing materials ranged between 1.8 and 5.4 mg/L for new and 30-year old copper, respectively. Good (1993) reported total zinc in first flush concentrations as high as 12,200 ug/L from industrial roofs in Washington state. Total zinc concentrations in steady-state runoff from galvanized surfaces have ranged from 438 ug/l in Malaysia (Yaziz et al., 1989) to 7,800 ug/L in Paris, France (Gromaire et al., 2004), with a median of the literature values reviewed of 2,400 ug/L.

Swiss authors reported that the rate of release (g/m²-yr) of zinc from zinc roofs was approximately 2 to 2.4 times higher than release of copper from copper roofing over a four-year study (Leuenberger-Minger et al., 2002). While copper and zinc roofs release high concentrations of copper or zinc, they have also been demonstrated to release other metals such as cadmium and lead (Sörme et al., 2001). Table A-2 summarizes literature values reported for total metals concentrations. The total metals concentrations listed in Table A-2 reflect total metals measured in steady-state runoff or event mean or median concentrations categorized by roofing material.

The metals loads leached from roofing strongly depend on the composition of the roofing; however, the addition of various chemicals may not affect the composition of the runoff in the anticipated fashion. Brunk et al. (2009) noted that the addition of metal alloys to metal roofing materials impacted the runoff in unexpected ways. They noted that although the bulk composition of a zinc and copper alloy was 15% zinc and 85% copper, the runoff composition from this roofing material was 57% zinc and 43% copper. Brunk's work confirmed the earlier two-year study of Herting et al. (2008) who noted that zinc was preferentially released from the brass in a process they termed called dezincification. Both sets of authors noted that the percent of a specific metal in alloys could not be used to predict the release of copper or zinc from pure metal sheets.

The metals loads leached from roofing also strongly depend on the composition of coatings that may be applied to the roof surface (i.e., sealants or coatings). For example, phosphated and chromated coatings have been demonstrated to reduce the concentrations of zinc substantially (Table A-2). Pre-painted zinc surfaces can result in concentrations that are two orders of magnitude below those from raw galvanized surface (Table A-2) (Robert-Sainte et al., 2009; Heijerick et al., 2002). Aluminum-zinc alloy products such as Galvalume® or Galfan® coated zinc) resulted in lower zinc concentrations in the runoff as well (Clark, 2010; Mendez et al., 2000; Heijerick et al., 2002). Persson and Kucera (2001) measured runoff from a painted steel

surface after four months of field exposure and reported zinc concentrations as high as 2,100 ug/L. This was likely a function of the composition of the zinc-containing paint.

The literature contains conflicting reports about the relationship between age of the roofing material and the amount of metal leached from it. Pennington and Webster-Brown (2008) reported lower concentrations of copper leaching from 37- and 45-year old copper roofs than from an 8-year old roof (Table A-2). Lindstrom et al. (2010) reported that zinc diminished with time over the first two years; Clark et al. (2008a) reported that age did not diminish the zinc reservoir available for leaching from galvanized roofing materials; and Robert-Sainte et al. (2009) found greater zinc loading associated with older zinc roofs in three different locations in Europe. Zinc roofs ranged in age from new to 145 years old. They reported that the runoff loading was similar regardless of age. In an earlier publication he reported that once the patina had aged, the dissolution and runoff of the metal was in steady-state with the metals in the patina (Odnevall Wallinder and Leygraf, 1997 and 19988).

Non-Metal Roofs

Concrete and ceramic tile roofs also contribute total metals, albeit at concentrations lower than those from galvanized or copper roofs (Table A-2). Persson and Kucera (2001) reported measurable concentrations of chromium, nickel, lead and zinc in runoff from concrete tiles (Table A-2). Elevated concentrations of cadmium and lead have been reported in tile roof runoff in Nigeria (Ayenimo et al., 2006). Sörme et al. (2001) also reported chromium concentrations emanating from concrete. Togerö (2006) conducted compositional analyses and leaching tests on concrete samples containing Portland cement, fly ash and slag. While both fly ash and slag have higher metals composition, leachate did not exhibit substantial differences. He also evaluated the impacts of additives to the concrete in 240-hour leaching tests with distilled water. He found that 71% of the added thiocyanate, 17% of the added resin acid, and 20-30% of the added nonylphenol oxalate leached from the mixtures. In Gdansk, Poland, Tobiszewski et al. (2010) reported PCBs in ceramic tile roof runoff at concentrations that ranged between 1,327 and 303 ug/L of PCB 52 in the first flush and between 131 and 565 ug/L for steady-state flows. It is unclear whether these PCBs were a result of aerial deposition or leaching from the material.

Asphalt shingle roofs have been reported to contribute lower zinc concentrations to the runoff than zinc roofs (Table A-2), but may have other contaminants that leach to stormwater. Clark (2010) and Mendez et al. (2000) reported measureable concentrations of arsenic from asphalt shingle roofs ranging from <0.01 to 1.4 ug/L. Mendez (2000) and Chang et al. (2004) measured both copper and lead in runoff from asphalt roofs. Roofs that have been impregnated with copper as a pesticide (Barron, 2000), or have a galvanized strip fastened across the roof line to reduce moss growth also release metals in runoff.

Non-metal roofs, such as built-up, flexible PVC, rubber, polyester, and gravel roofs have been shown to release lower concentrations of metals than metal roofs (Table A-2). Good (1993) reported that built up roof contributed 166 ug/L of copper, which was approximately ten times the concentration from other roofing materials he evaluated. Björklund (2011) cited literature reporting cadmium, lead, and zinc release from PVC plastics. In addition, these roofs may release other contaminants of concern.

Built-up roofs (BUR), which are common on industrial and commercial buildings, are comprised of layers of bituminous materials (asphalt or coal tar) and roof felts which serve as a moisture barrier. In a study of road surface sealants, Mahler et al. (2012) demonstrated that coal tar released 1,000 times higher concentrations of PAHs than did asphalt sealants. Coal tar applied to built-up roofs may be expected to leach more readily than from asphalt applications. In a leaching test simulating rain, Clark et al. (2008a) reported that roofing felt exposed to a leaching test resulted in bis (2-ethylhexyl) phthalate (DEHP) at a concentration of 315 ug/L.

DEHP is a plasticizing agent found not only in roofing felt, but also in PVC and other synthetic roofing materials. Pitt et al. (2000) conducted simulated rain leaching tests on construction materials and found that DEHP was released from PVC and Plexiglass. Pastuska (1985) reported that PVC plastic sheeting 0.8 mm thick lost 8% of its plasticizers over 18 years, while the same material covered with gravel lost 16% over 9 years. In cooler climates this loss is thought to be through migration and washout rather than volatilization. Synthetic roofing materials such as thermoplastic polyolefin (TPO) roofing, Cool roofs, and ethylene propylene diene monomer (EPDM or rubber roofing) may also contain and release phthalates. Björklund (2010) found measurable concentrations of several other phthalates [DEHP, diisononyl phthalate (DINP), diisodecyl phthalate (DIDP) and di-n-butyl phthalate (DBP)] and nonylphenolic compounds were released from roofing and cladding in Sweden. Her mass balance showed that two-thirds of the DBP budget was due to releases from roofing and cladding.

Untreated wood shingle roofs have been demonstrated to release low concentrations of arsenic copper, lead, and zinc (Table A-2). Treated wood shingles also leach these compounds as well as other compounds (Table A-2). In leaching tests, Pitt et al. (2000) measured phthalates, pesticides, and other volatile compounds in untreated plywood. Wood shingles treated with copper can result in copper concentrations in the runoff reported as high as 1.9 million ug/L (Clark, 2010). Persson and Kucera (2001) reported copper concentrations in runoff from copper-impregnated wood between 1,150 and 4,050 ug/L. The differences between these two studies may reflect process differences between the U.S. and Sweden or between specific manufacturers. Kahn et al. (2006) evaluated chromated-copper-arsenate (CCA)-treated wood and found arsenic concentrations averaging 600 ug/L in leachate from decking materials. CCA-treated shingles could also be expected to release arsenic, copper, and chromium to stormwater, even though a sloped roof would provide less retention time that decking materials. Copper-containing granules are also impregnated into asphalt shingles to resist the growth of algae that can discolor roofs. The granules which are designed to release copper over the life of the roof, have been calculated to release between 560 and 640 ug/L of copper oxide (Everman and Joedicke, 2006).

Roofing materials may also be treated with numerous other biocides to extend the useful life of the materials. Bucheli et al. (1998) found the herbicide (R,S) mecoprop in leachate from a bituminous under layer of a flat vegetated roof that was treated with the herbicide to avoid penetration by plant roots. Burkhardt et al. (2007) evaluated runoff from building materials including roofing. They found four biocides (terbutryn, carbendazim, mecoprop, and Irgarol 1051) in roofing materials runoff that exceeded the Swiss water quality standards. They also tested 16 bituminous sheets and found the concentrations of mecoprop in the synthetic rain leachate (7-day leaching) varied by two orders of magnitude, depending on the brand. Jungnickel et al. (2008) evaluated biocides leaching from German roof paints and found that

peak concentrations ranged from 0.1 to 5.2 mg/L depending on rain intensity and duration. They pointed out that the paint labels did not always correspond to the biocides measured.

Vegetated Roofs

Vegetated roofs can also contribute heavy metals and other pollutants to runoff. Alsup et al. (2011) reported elevated concentrations of cadmium (20 ug/L), lead (64 ug/L), and zinc (624 ug/L) in leachate from vegetated roofs that had been established for 22 months. The concentrations of cadmium and zinc declined over the 10-month study period. Metals may have leached from the construction materials, the soil matrix, or the fertilizer that was applied shortly before the first sampling. Clark et al. (2008b) reported much lower concentrations (copper at concentrations less than 30 ug/L and zinc at concentrations less than 250 ug/L) from vegetated roof plots. The composition of the soil medium, understructure, and drainage layers can impact the stormwater that leaches through and runs off. Moran et al. (2005) reported that nitrogen and phosphorus were leached from a soil matrix composed of 15% compost. Long et al. (2006) suggested that because the soil matrix represents the greatest volume of vegetated roof structure, proper pre-testing and selection of a medium can improve runoff quality.

Other Factors Affecting Contaminants in Roof Runoff

In addition to the composition of the roof, a number of factors influence the concentrations of contaminants in the roof runoff. The most prominent factor is the pH of the rain. As pH decreases (greater acidity), metal solubility increases, and the metals concentrations in runoff also increase. He et al. (2001) reported an increase in the amounts of copper and zinc released during both first flush and steady-state runoff with decreasing pH. They attributed this result to the greater solubilization of copper and zinc corrosion products at lower pH. Bielmyer et al. (2012) also evaluated the impacts of pH using simulated rainwater. At pHs of 4.5 and 5.8 the median total copper concentrations measured were 433 and 76 ug/L for copper panes of the same length. Odnevall Wallinder et al. (2002) investigated release rates from stainless steel under different pH regimes. They found that the release rate of chromium was ten times and the release rate of nickel was three to four times greater at a pH of 4.3 than at a pH of 5.7. Odnevall Wallinder et al. (2004) demonstrated that the pH of the rain had a dominating effect on the dissolution of copper corrosion products, whereas nitrate in rainwater had a smaller and inhibiting impact, and chloride and sulfate concentrations had no significant effect.

Odnevall Wallinder et al. (1998) identified that metal corrosion rates were a function of the air pollutant sulfur dioxide concentrations. Since they also reported that runoff rates are a function of the corrosion rate, they measured significantly higher runoff loads in the highly industrialized areas of Belgium than in Stockholm. They noted at the end of the article that since SO_2 concentrations had been reduced under more recent environmental regulations, corrosion rates and therefore runoff loads were generally lower than 50 years ago.

Marine environments which contain sea salt aerosols had a surprising effect of reducing the annual release of copper in runoff compared to a more urban inland environment when standardized for rainfall depth Sandberg et al. (2006). The authors attributed this effect to long

periods of wet conditions and higher humidity in the marine environment and less frequent wet and dry cycles for dissolution and re-precipitation processes than found at the inland site. Authors have reported that the metals in roof runoff were predominantly in the dissolved phase. Golding (2006) reported between 70 and 100% of the zinc from metal and PVC roofs was in the dissolved phase. Heijerick et al. (2002) calculated that between 96 and 99.9% of the zinc from zinc roofs was in the dissolved phase. Athanasiadis et al. (2004) reported that 97% of the zinc in zinc roof runoff was in the dissolved phase. Förster (1996) reported dissolved copper in runoff from copper roofs predominated at rain pH values less than 6.0. Dissolved metals are more mobile in the environment than particulate metals.

He et al. (2001) reported a relationship between precipitation intensity and loading from copper roofs. At low intensity rain (drizzle or 1 mm/hr), copper loading increased more rapidly with accumulated volume than for light rain (8 mm/hr) or moderate rain (20 mm/hr). This is in line with the work by Odnevall Wallinder and Leygraf (2001) who reported that copper corrosion rates were a function of relative humidity; and drizzle is often associated with highly humid air. He et al. (2001) observed no differences between the 8 mm and 20 mm precipitation intensities.

Additionally, these authors demonstrated that copper and zinc runoff loading in terms of ug/m^2 of roof was a function of precipitation depth. Junknickel et al. (2008) identified a relationship between intensity and duration. They reported substantially lower peak concentrations of biocides leached from a 40 mm/hr precipitation intensity within 2 hours (0.1 ug/L) than leached from a 0.3 mm/hr intensity (0.9 to 5.2 mg/L) in synthetic rain-simulated runoff trials.

Residence time of the precipitation on the roofing materials can also influence the metals concentrations in runoff. Odnevall Wallinder et al. (2000) reported that the slope of the roof drastically affects the contaminant load from a roof. When exposed to vertical precipitation (i.e., windless conditions), steeper roofs have less exposed surface area (as projected onto a horizontal surface) in contact with the rain. They noted that less vertical precipitation impinges on steeper roofs, and less volume accumulates from steeper roofs under windless conditions. Concentration of contaminants in the runoff may also be a function of the contact time between the roof and a raindrop; thus that shallower sloped roofs would allow longer contact time with the precipitation. Arnold (2005) successfully included a correction factor for roof slope in his model as a simple cosine of the angle of roof inclination. Recently, Bielmyer et al. (2012) observed that concentration of copper was a function of the median run length of the raindrops, and was thus related to the length of the copper panel.

Odnevall Wallinder et al. (2000) found that metals loading in runoff from roofs was also a function of the direction of the prevailing wind, as a greater volume of rain actually hits the surfaces facing the prevailing direction.

Aerial Deposition

Contaminants associated with wet and dry air deposition comprise a portion of roof runoff. For example, Sabin et al. (2005) found that more than 50% of the metals in stormwater runoff in Los Angeles were associated with air deposition. In a Swiss study, the ratio of the concentrations of metals in runoff compared to wet and dry atmospheric deposition ranged from as high as 27:1 for copper to less than 1:1 for zinc depending on the roofing type and the location (Zobrist et al.,

2000). Förster (1998) found elevated polycyclic aromatic hydrocarbon (PAH) concentrations in winter roof runoff which he associated with combustion products from heating in Bavaria, Germany. The quantity of atmospheric deposition depends on the amount and types of air pollutants emitted in the vicinity and upwind of a site (Förster, 1998), and the length of time between precipitation events (Thomas and Greene, 1993). For example, Line et al. (1997) found higher concentrations of metals in runoff from industries, such as wood preservers, that had exposed metals stored on site or within the product. A recent study of the Puget Sound Basin evaluated heavy metals, PAHs, and other compounds in wet and dry atmospheric deposition. This study found that concentrations of the chemicals of concern in the highly urbanized area sampled were an order of magnitude greater than outside the urban area (Brandenberger et al., 2011). The relative contribution of pollutants associated with wet and dry deposition has not been compared to concentrations in runoff from roofing materials within the Puget Sound Basin.

While wet and dry air deposition contributes to the contaminants from commercial, residential, and industrial roofs, researchers have found that roof composition also plays a dominant role in the contaminants that are released from roofing materials in runoff. Pitt et al. (2000) demonstrated the leaching of metals, PAHs, phthalates, pesticides, and other compounds from the construction materials themselves. Clark et al. (2003) performed similar leaching tests which simulated exposure to rainwater. Their research confirmed the leaching of constituents as a function of material composition. To differentiate between materials leaching and air deposition, recent studies have attempted to control for the contribution of air deposition, thereby evaluating the concentrations that leach from the roofing materials themselves. Chang and Crowley (1993) measured and subtracted only wet deposition; and their results may have been affected by dry deposition of metals from a local fertilizer manufacturer. Clark (2010) and Chang et al. (2004) considered both wet and dry aerial deposition.

	T /•			ug/L			pH of	A 41			
Roof Type	Location	As	Cd	Cu	Pb	Zn	rain	Author			
Zinc Roofs											
Zinc	Paris, France					7,800		Gromaire et al. (2002)			
New Zinc	Paris, France		ND	ND	0.5	6,064		Robert-Saint et al. (2009)			
Old Zn - 40 yrs old	Paris, France		3.2	2.2	30.2	7,080		Robert-Saint et al. (2009)			
General galv steel (hot dipped)	Sweden					5,500	6.3	Hiejerick et al. (2002)			
Galvanized iron	Malaysia				199	423	6.6	Yaziz et al. (1989)			
Galvanized iron - galv gutter (wet & dry deposition subtracted from results)	Texas			ND	ND	8,134	5.5	Chang et al. (2004)			
Metal - old and maybe coated with Al paint	Washington			4	8	1,040		Good (1993)			
Steel with Zn coating	Paris, France		ND	ND	0.3	3,081		Robert-Saint et al. (2009)			
			Treat	ted Zinc Ro	oofs						
Galvalume (55% Al, Zn coated steel)	Pennsylvania	ND	1.3	ND	2.1	24.8	4.3	Clark (2010)			
Galvalum	Texas	< 0.29	<0.10	2.2	0.7	118	6	Mendez et al. (2000)			
Galvalum	Sweden					1,600	5.8	Hiejerick et al. (2002)			
Galfan (Al coated)	Sweden					1,600	5.9	Hiejerick et al. (2002)			
Galfan + TOC top coating	Sweden					700	5.9	Hiejerick et al. (2002)			
Zinc Anthra (phosphated Zn product)	Sweden					2,300	6	Hiejerick et al. (2002)			
Anthra metal with Zn(PO4)2 coalting	Paris, France		ND	0.1	1.1	3597		Robert-Saint et al. (2009)			
Zinc Quartz (phosphated Zn product)	Sweden					2,500	6	Hiejerick et al. (2002)			

Table A-2. Concentrations of total metals measured in roof runoff from studies of various roof types.

D. CT	T (•			ug/L			pH of	
Roof Type	Location	As	Cd	Cu	Pb	Zn	rain	Author
Galvanized steel + Cr seal	Sweden					2,400	6	Hiejerick et al. (2002)
Galvanized steel + TOC	Sweden					1,200	5.7	Hiejerick et al. (2002)
Prepainted galvanized steel	Sweden					160	5.4	Hiejerick et al. (2002)
Painted steel	Sweden					2,100		Persson & Kucera (2001)
Prepainted galv steel. Stainless with Zn coating and polyester top coat	Paris, France		ND	2.9	0.5	31		Robert-Saint et al. (2009)
			Othe	r Metal Ro	ofs			-
Sheet metal	Nigeria		450		810	160		Ayenimo et al. (2006)
Stainless steel	Paris, France		ND	0.6	0.4	39		Robert-Saint et al. (2009)
Aluminum	Paris, France		ND	0.2	3.5	37		Robert-Saint et al. (2009)
Corrugated aluminum	Pennsylvania	ND	0.2	ND	6.1	5,751	4.3	Clark (2010)
Aluminum galv gutter (wet & dry deposition subtracted from results)	Texas			26	37	2,163	5.5	Chang et al. (2004)
Copper	Sweden			3,575				Persson & Kucera (2001)
Copper 8 years old	New Zealand			1,976			6.45 - 7.76	Pennington & Webster-Brown (2008)
Copper 11 years old	Connecticut			2,660		31	6.2	Boulanger & Nikolaidis (2003)
Copper 37 years old	New Zealand			1,000			6.45 - 7.76	Pennington & Webster-Brown (2008)
Copper 45 years old	New Zealand			1,172			6.45 - 7.76	Pennington & Webster-Brown (2008)
Copper 72 years old	Connecticut			1,460				Boulanger & Nikolaidis (2003)
				File Roofs				
Concrete tile	Texas	0.42	< 0.10	5.3	1.3	91	6	Mendez et al. (2000)
Concrete tile	Malaysia				197	94	6.9	Yaziz et al. (1989)
Concrete tile	Sweden			<20	3.5	25		Persson & Kucera (2001)

Table A-2. Concentrations of total metals measured in roof runoff from studies of various roof types.

	т			ug/L			pH of	A 41
Roof Type	Location	As Cd Cu		Pb	Zn	rain	Author	
Clay tile	Switzerland			71	13	10		Zorbrist et al. (2000)
Clay tile (wet depostion subtracted from results)	Texas				ND	320		Chang & Crowley (1993)
Ceramic tile	Nigeria		550		1,110	850		Ayenimo et al. (2006)
			Sh	ingle Roofs	8			
Asphalt Shingles	Pennsylvania	0.3	ND	ND	ND	ND	4.3	Clark (2010)
Asphalt shingle - galv gutter (wet & dry deposition subtracted from results)	Texas			ND	ND	554	5.5	Chang et al. (2004)
Asphalt fiberglass shingles	Texas	< 0.29	< 0.10	25.7	0.6	28.2	6.7	Mendez et al. (2000)
Asphalt - Residenital						149.0		Bannerman et al. (1993)
Asphalt - Residenital	Michigan & Wisconsin			0.7	10	318		Steuer et al. (1997)
			Syn	thetic Roo	fs			
Corrugated PVC	Pennsylvania	0.1	ND	ND	0.1		4.3	Clark (2010)
Rubber Roofing	Pennsylvania	ND	1.9	ND	1.3	94	4.3	Clark (2010)
Ondura	Pennsylvania	ND	ND	ND	0.2	115	4.3	Clark (2010)
Cool	Texas	< 0.29	< 0.10	1.3	0.6	46	6	Mendez et al. (2000)
Polyester	Switzerland			217	4.9	27		Zorbrist et al. (2000)
		Built	t-Up and C	ther Instit	uional Ro	ofs		
Built-up commercial	Wisconsin			9	7	330		Bannerman et al. (1993)
Built-up industrial	Wisconsin			6	8	1,155		Bannerman et al. (1993)
Built-up commercial	Michigan & Wisconsin			0.9	23	348		Steuer et al. (1997)
Gravel	Switzerland			18	2.7	9		Zorbrist et al. (2000)
Roofing Felt	Pennsylvania	0.3	0.3	ND	1.1	ND	4.3	Clark (2010)
		V	Vood and 7	reated W	ood Roofs			

Table A-2. Concentrations of total metals measured in roof runoff from studies of various roof types.

DÍT	T /·			ug/L			pH of	A . / T
Roof Type	Location	As	Cd	Cu	Pb	Zn	rain	Author
Wood shingle (galvanized gutter) (wet & dry depostion subtracted from results)	Texas			1	ND	9,632	5.5	Chang et al. (2004)
Cedar Shakes	Pennsylvania	ND	ND	ND	0.8	201	4.3	Clark (2010)
Untreated wood	Florida	2						Khan et al. (2006)
Untreated plywood	Pennsylvania	ND	0.1	ND	1.6	ND	4.3	Clark (2010)
CCA treated wood	Florida	600					4.5	Khan et al. (2006)
Pressure Treated/Water Sealed Wood	Pennsylvania	4.2	0.0	1,867,020	ND	890	4.3	Clark (2010)
Pressure Treated Wood	Pennsylvania	1.3	0.1	1,690,794	ND	ND	4.3	Clark (2010)
Impregnated wood - new	Sweden			4,050				Persson & Kucera (2001)
Impregnated wood - 9-12 months old	Sweden			1,150				Persson & Kucera (2001)

Table A-2. Concentrations of total metals measured in roof runoff from studies of various roof types.

References for Appendix A

Alsup, S.E., S.D. Ebbs, L.L. Battaglia, ad W.A. Retzlaff. 2011. Heavy metals in leachate from simulated green roof systems. Ecological Engineering. 37: 1709-1717.

Athanasiadis, K., B. Helmreich, and P.A. Wilderer. 2004. Elimination of Zinc from roof runoff through geotextile and clinoptilolite filers. Acta Hydrochim. Hydrobiol. 32(6): 419-428.

Arnold, R. 2005. Estimations of copper roof runoff rates in the United States. Integrated Environmental Assessment and Management. 1(4): 333-342.

Ayenimo, J.G., A.S. Adekunle, W.O. Makinde, and G.O. Ogunlusi. 2006. Heavy metal fractionation in roof run off in Ile-Ife, Nigeria. International Journal of Environmental Science and Technology. 3(3): 221-227.

Bannerman, R., K. Baun, M. Bohn, P. Hughes, and D.A. Graczyk. 1983. Evaluation of Urban nonpoint source pollution management in Milwaukee County Wisconsin. U.S. Environmental Protection Agency Publication No 84-114164.

Bannerman, R.T., D.W. Owens, R.B. Dodds, and N.J. Hornewer. 1993. Sources of pollutants in Wisconsin stormwater. Water Science & Technology. 28 (3-5): 241-259.

Bielmyer, G.W., W.R. Arnold, J.R. Tomasso, J.J. Isely, and S. J. Klaine. 2011. Effects of roof and rainwater characteristics on copper concentrations in roof runoff. Environmental Monitoring and Assessment. 184: 2797-2804.

Björklund, K. 2011. Sources and fluxes of organic contaminants in urban runoff. Ph.D. Thesis. Chalmers University of Technology, Gothenburg, Sweden.

Björklund, K. 2010. Substance flow analyses of phthalates and nonylphenols in stormwater. Water Science & Technology. 48: 1154-1160.

Boller, M. 1997. Tracking heavy metals reveals sustainability deficits of urban drainage systems. Water Science & Technology. 35(9):77-87.

Brandenberger, J.M., P. Louchouarn, L-J Kuo, E.A. Crecelius, V. Cullinan, G.A. Gill, C. Garland, J. Williamson, and R. Dhammapala. 2011. Control of Toxic Chemicals in Puget Sound, Phase 3: Study of Atmospheric Deposition of Air Toxics to the Surface of Puget Sound. Prepared for Department of Ecology. Publication No. 10-02-012.

Brunk, J., D. Lindström, and S. Goidanich, and I. Odnevall Wallinder. 2009. On-going activities at KTH (Royal Institute of Technology Stockholm, Sweden) 2009. Presented in Brussels, Belgium, October 16, 2009.

Bucheli, T.D., S.R. Muller, and A. Voegelin. 1998. Bituminous roof sealing membranes as major sources of the herbicide (R,S)-mecoprop in roof runoff waters: potential contamination of groundwater and surface waters. Environmental Science & Technology. 32 (21): 3465-3471.

Burkhardt M, T. Kupper, S. Hean, R. Haag, P. Schmid, M. Kohler, and M. Boiler. 2007. Biocides used in building materials and their leaching behavior to sewer systems. Water Science & Technology. 56(12): 63-67.

Chang, M. and C.M. Crowley. 1993. Preliminary observations on water quality of storm runoff from four selected residential roofs. Water Resources Bulletin. 29: 777-783.

Chang, M., M. McBroom, and R. Beasley. 2004. Roofing as a source of nonpoint pollution. Journal of Environmental Management. 72: 307-315.

Clark, S. 2010. Unpublished Data. Pennsylvania State University, Harrisburg, PA.

Clark, S.E., B.V. Long, C.Y.S. Siu, J. Spicher and K.A. Steele. 2008b. Runoff quality from roofing during early life. WEFTEC 2008 Conference Proceedings, Chicago, IL. Water Environment Federation.

Clark, S.E., K.A. Steele, J. Spicher, C.Y.S. Siu, M.M. Lalor, R. Pitt, and J.T. Kirby, J.T. 2008a. Roofing materials' contributions to storm-water runoff pollution. Journal of Irrigation and Drainage Engineering. 34(5), 638-645.

Clark, S.E., M.M. Lalor, R. Pitt, and R. Field. 2003. Investigation of Wet-Weather Pollution Contribution from Building Materials Commonly Used at Industrial Sites. Presented to: 9th Annual Industrial Waste Conference, April 16, 2003.

Davis AP, M. Shokouhian, and S.Ni. 2001. Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. Chemosphere. 44(5): 997-1009.

Eriksson E. 2002. Potential and problems related to reuse of water in households. PhD Thesis. Environment & Resources, Technical University of Denmark, Kgs. Lyngby, Denmark.

Everman, R.L. and I.B. Joedicke. 2006. Algae-resistant roofing granule copper release. White paper provided to the Biocides Panel, Copper Reregistration Task Force, American Chemical Society. March 27, 2006.

Förster, J. 1998. The influence of location and season on the concentrations of macroions and organic trace pollutants in roof runoff. Water Science & Technology. 38(10): 83-99.

Förster, J. 1996. Patterns of roof runoff contamination and their potential implications on practice and regulation of treatment and local infiltration. Water Science & Technology. 33(6): 39-48.

Golding, S., 2006. A survey of zinc concentrations in industrial stormwater runoff. Washington State Department of Ecology, Olympia, WA. Publication No. 06-03-009. 36 pages + appendices. <u>https://fortress.wa.gov/ecy/publications/SummaryPages/0603009.html</u>

Good, J., 1993. Roof runoff as a diffuse source of metals and aquatic toxicity in stormwater. Water Science & Technology. 28 (3-5): 317-321.

Gromaire, M.C., G. Chebbo, and A. Constant, A. 2002. Impact of zinc roofing on urban runoff pollutant loads: The case of Paris. Water Science & Technology. 45(7) 113-122.

He, W., I. Odnevall Wallinder, and C Leygraf. 2001. A laboratory study of copper and zinc runoff during first flush and steady-state conditions. Corrosion Science. 43: 127-146.

Heijerick, D.G., C.R. Janssen, C. Karlén, I. Odnevall Wallinder, and C. Leygraf, C. 2002. Bioavailability of zinc in runoff water from roofing materials. Chemosphere. 47(10), 1073-1080.

Herting, G. S. Goidanich, I. Odnevall Wallinder, and C. Leygraf. 2008. Corrosion-induced release of Cu and Zn into rainwater from brass, bronze, and their pure metals. A 2-year field study. Environmental Monitoring and Assessment. 44: 455-461.

Jungnickel, C. F. Stock, T. Brandsch, and J. Ranke. 2008. Risk assessment of biocides in roof paint. Part 1: experimental determination and modeling for biocide leaching from roof paint. Environmental Science Pollution Resources 15(3): 258-265.

Karlén, C. I. Odnevall Wallinder, D. Heijerick, and C. Leygraf. 2002. Runoff rates, chemical speciation and bioavailability of copper released from naturally patinated copper. Environmental Pollution 120:691-700.

Lindstrom, D., Y. Hedberg, and I. Odnevall Wallinder. 2010. Chromium (III) and chromium (VI) surface treated galvanized steel for outdoor constructions: Environmental Aspects. Environmental Science & Technology. 44(11): 4322-4327.

Line, D.E., J. Wu, J.A. Arnold, G.D. Jennings, and A.R. Rubin. 1997. Water quality in the first flush runoff from 20 industrial sites. Water Environment. May/June: 305-310.

Long, B.V., Clark, S.E. Baker, and R. Berghage. 2006. Green roof media selection for minimization of pollutant loadings in roof runoff. WEFTEC 2006 Conference Proceedings, Dallas, TX. Water Environment Federation.

Leuenberger-Minger, A.U., M. Faller, and P.Richner. 2002. Runoff of copper and zinc caused by atmospheric corrosion. Materials and Corrosion. 53: 1567-164.

Lye, D. 2009. Rooftop runoff as a source of contamination: A review. Science of the Total Environment. 407: 5429-5434.

Mahler, B.J., P.C. Van Metre, J.L. Crane, A.W. Watts, M. Scoggins, and E.S. Williams. 2012. Coal-tar-based pavement sealcoat and PAHs: Implications for the environment, human health, and stormwater management. Environmental Science & Technology. 46: 3039-3045.

Mendez, C.B., B.R. Afshar, K. Kinney, M.E. Barrett, and M.J. Kirisits. 2000. Effect of roof material on water quality for rainwater harvesting systems. Texas Water Development Board, Austin, TX.

Moran A, B. Hunt, and J. Smith J. 2005. Hydrologic and water quality performance from greenroofs in Goldsboro and Raleigh, North Carolina. Paper presented at the Third Annual Greening Rooftops for Sustainable Communities Conference, Awards and Trade Show; 4-6 May 2005, Washington, DC.

NADP. 2012. National Atmospheric Deposition Program. Chemical data from 2000 through 2010 accessed for the following five stations: Olympic National Park – Hoh Ranger Station, Mount Rainier National Park – Tahoma Woods, North Cascades National Park – Marblemont Ranger Station, Le Grande, and Columbia River Gorge. Website accessed July 10, 2012. http://nadp.sws.uiuc.edu/sites/sitemap.asp?state=wa

Odnevall Wallinder, I and C. Leygraf. 1997. A study of copper runoff in an urban atmosphere. Corrosion Science. 29(12): 2039-2052.

Odnevall Wallinder, I. and C. Leygraf. 1998. The influence of patina age and pollution levels on the runoff rate of zinc from roofing materials. Corrosion Science. 40(11): 1977-1982.

Odnevall Wallinder, I., P. Verbiest, W. He, and C. Leygraf. 2000. Exposure direction and inclination on the runoff rates of zinc and copper roofs. Corrosion Science. 42: 1471.

Odnevall Wallinder, I. and C. Leygraf. 2001. Seasonal variations in corrosion rate and runoff rate of copper roofs in an urban and rural atmospheric environment. 43: 2379-2396.

Odnevall Wallinder, I., J.Lu, S. Bertling, and C. Leygraf. 2002. Release rates of chromium and nickel from 304 and 316 stainless steel during urban atmospheric exposure – a combined field and laboratory study. Corrosion Science 44: 2303-2319.

Odnevall Wallinder, I.O., S. Bertling, X. Zhang, and C. Leygraf. 2004. Predictive models of copper runoff from external structures. Journal of Environmental Monitoring. 6: 704-712.

Pastuska, Gerhard. 1985. Roof coverings made of PVC sheetings: The effect of plasticizers on lifetime and service performance. Proceedings of the 2nd International Symposium on Roofing Technology, National Roofing Construction Association, Rosemont IL, Sept. 1985. 173-176.

Pennington, S. and J. Webster-Brown. 2008. Stormwater runoff from copper roofing, Auckland, New Zealand. New Zealand Journal of Marine and Freshwater Research, 42: 99-108.

Persson, D. and V. Kucera. 2001. Release of Metals from Buildings, Constructions and Products during Atmospheric Exposure in Stockholm. Water, Air, and Soil Pollution Focus. 1(3): 133-150.

Pitt, R. and M. Lalor. 2000. Module 4d: The role of pollution prevention in stormwater management. Presented at the 2000 Conference on stormwater and Urban Water Systems Modeling. Toronto, Canada. February 24-25.

Pitt, R. Pitt, R., M. Lilburn, S. Nix, S.R. Durrans, S. Burian, J. Voorhees, and J. Martinson. 2000. Guidance Manual for Integrated Wet Weather Flow (WWF) Collection and Treatment Systems for Newly Urbanized Areas (New WWF Systems). U.S. Environmental Protection Agency. 612 pgs.

Quek, U. and J. Förester. 1993. Trace metals in roof runoff. Water, Air, and Soil Pollution. 68: 373-389.

Robert-Sainte, M.C. Gromaire, B. DeGouvello, M. Saad, and G. Chebbo. 2009. Annual metallic flows in roof runoff from different materials: test-bed scale in Paris conurbation. Environmental Science & Technology. 43 (15): 5612-5618.

Sabin, L.D., J.H. Lim, K.D. Stolzenbach, and K.C. Schiff. 2005. Contribution of trace metals from atmospheric deposition to stormwater runoff in a small impervious urban catchment. Water Research. 39(16):3929-2937.

Sandberg, J., I. Odnevall Wallinder, C. Leygraf, and N. LeBozec. 2006. Corrosion-induced copper runoff from naturally and pre-patinated copper in a marine environment. Science Corrosion Science 48:4316-4338.

Sörme L, Bergbäck B and Lohm U (2001) Goods in the Anthroposphere as a Metal Emission Source - A Case Study of Stockholm, Sweden. Water, Air, and Soil Pollution: Focus. 1(3): 213-227.

Steuer, J., W. Selbig, N. Hornewer, and J. Prey. 1997. Sources of Contamination in an Urban Basin in Marquette, Michigan and an Analysis of Concentrations, Loads, and data Quality. United States geological Survey, Water-resources Investigations Report 97-4242. 25 pages.

Tobiason, S. 2004. Stormwater metals removed by media filtration: Field assessment case study. Watershed 2004 Conference Proceedings, Water Environmental Conference, Alexandria, VA.

Tobiszewski, M., S. Polkowska, P. Konieczka, and J. Namiesnik. 2010. Roofing materials as pollution emitters – concentration changes during runoff. Polish Journal of Environmental Studies. 19(5): 1019-1028.

Togerö, Å. 2006. Leaching of hazardous substances from additives and admixtures in concrete. Environmental Engineering Science. 23(1): 102-118.

Yaziz, M.I., H. Gunting, N. Sapari, and A.W. Ghazali, 1989. Variations in rainwater quality from roof catchments. Water Research. 23 (6):761-765.

Zobrist, J., S.R Muller, and T.D. Bucheli. 2000. Quality of roof runoff for groundwater infiltration. Water Resources. 34: 1455.

Appendix B. List of Roofing Task Force October 24, 2012 Meeting Participants

Company/Association/Agency	First Name	Last Name	Telephone Number	Email Address	Participation in Oct 24, 2012 meeting
3M	Jeff	Jacobs	919-691-2073	jljacobs@mmm.com	
3M	Frank	Klink	Office: 651 733 0099 Mobile: 651 283 1876	<u>fwklink@mmm.com</u>	х
3M	Wayne	Neumann	651-733-4648	whneumann1@mmm.com	Х
Akzo Nobel Coatings Inc /Metal Alliance	Edward	Karper	614-298-1883	Ed.Karper@akzonobel.com	Х
ARMA	Mike	Fischer	315-420-8208	MFischer@kellencompany.com	Х
Asphalt Roofing Manufacturers Association (ARMA)	John	Ferraro	202-207-1121	JFerraro@kellencompany.com	х
Cedar Shake and Shingle Bureau	Peter	Parmenter	912-898-8173	peter@cedarbureau.com	
Cedar Shake and Shingle Bureau	Lynne	Christiansen	604-820-7700	lynne@cedarbureau.com	
CertainTeed	Steve	Johnston	503-243-5238	stephen.d.johnston@saint-gobain.com	Х
Champion Metal of Washington	John	Devore	425-485-3003	John@championmetal.com	
Chemical Fabrics and Films Association (CFFA)/Duro-Last Roofing	Kevin	Kelley	800-248-0280	KKelley@duro-last.com	х
Copper Development Association Inc.	Joseph	Gorsuch	Office: 585.545.4805 Mobile: 585.217.3904	joseph.gorsuch@copperalliance.us	х
Copper Development Association Inc.	Wayne	Seale	425-793-6306	wayne.seale@copperalliance.us	
Duwamish River Cleanup Coalition	Heather	Trim	206-351-2898	heatrim@gmail.com	Х
Ecology	Alli	Kingfisher	509-329-3448	agra461@ecy.wa.gov	
Ecology	Dale	Norton	360-407-6765	dnor461@ecy.wa.gov	Х
Ecology	Nancy	Winters	360-407-7392	nwin461@ecy.wa.gov	Х
IB Roof Systems	Shawn	Stanley	541-543-7889	shawndstanley@gmail.com	Х
International Zinc Association	Eric	Van Genderen	919-361-4647 ext. 3014	evangenderen@zinc.org	
King County Natural Resources	David	Batts	206 296-1123	David.Batts@kingcounty.gov	Х
Malarkey Roofing	Mike	Tuel	503-283-1191	mtuel@malarkeyroofing.com	Х
Malarkey Roofing	Greg	Malarkey	503-283-1191	gmalarkey@malarkeyroofing.com	Х
Malarkey Roofing	Joe	Russo	425-418-3456	joe.malarkey@yahoo.com	Х
Metal Construction Alliance	Scott	Kriner	610-966-2430	skriner1@verizon.net	Х
National Roofing Contractors Association	Mark	Graham	847-493-7511	mgraham@nrca.net	Х

Company/Association/Agency	First Name	Last Name	Telephone Number	Email Address	Participation in Oct 24, 2012 meeting
(NRCA)					
Northwest EcoBuilding Guild	Howard	Thurston	503-459-2552	ht_pe@earthlink.net	Х
Owens Corning Asphalt Technology Lab	Dave	Trumbore	Mobile: 773-746-7278 Office: 708-594-6980	dave.trumbore@owenscorning.com	
Pabco Roofing Products	Trevor	Bingham	253-284-1228	Trevor.Bingham@paccoast.com	Х
Pabco Roofing Products	Sid	Dinwiddie	253-284-1255	Sid.Dinwiddie@paccoast.com	Х
Pacific Northwest Pollution Prevention Resource Center	Brian	Penttila	206.352.2050	bpenttila@pprc.org	
Polyglass USA	Mike	Griffin	253-389-8099	mgriffin@polyglass.com	Х
Polyglass USA	Rod	Pierce	503-830-3661	brotherspierce@yahoo.com	
Puget Sound Partnership	Scott	Redman	360.464.1230	scott.redman@psp.wa.gov	
Schacht Aslani Architects	Neil	Parrish	615-830-5600	Neil@saarch.com	Х
Single Ply Roofing Institute (SPRI)	Steve	Graveline		Graveline.stan@us.sika.com	
Single Ply Roofing Institute (SPRI)	Paul	Riesebieter	Mobile: 360-601-3661	paul.riesebieter@jm.com	Х
Specialty Granules, Inc.	Ingo	Joedicke	301-714-1481	ijoedicke@specialtygranules.com	
Steelscape	Renee	Ramey	360-673-8236	renee.ramey@steelscape.com	Х
Stoel Rives	Lincoln	Loehr	206 386-7686	lcloehr@stoel.com	Х
The Boeing Company	Roy	Cargo		roy.j.cargo@boeing.com	
Tile Roofing Institute (TRI)	Rick	Olson	541-689-0366	rolson@tileroofing.org	
United Coatings/Quest CP	Stephen	Heinje	509-991-0752	heinje@quest-cp.com	Х
Washington Environmental Council	Bruce	Wishart	360-223-2033	wishart.bruce@comcast.net	Х
Western Wood Preservers Institute	Dallin	Brooks	360-693-9958	dallin@wwpinstitute.org	
Windward Environmental	Scott	Tobiason	206 812-5424	scottt@windwardenv.com	Х
WSU Stormwater Center	Lisa	Rozmyn	253-445-4552	lisa.rozmyn@wsu.edu	Х

Appendix C. Roofing Assessment Procedures

Decontamination Procedures

Panels

Following construction of the pilot-scale roofing panels, panels will be covered with plastic sheeting until decontamination, when the plastic sheeting will be removed. Each panel will be decontaminated to remove any contaminants from transportation and construction processes. Each panel will be rinsed for approximately 10 minutes with tap water applied from the steeper end of the panel. Each panel will then be rinsed with approximately one gallon of distilled deionized water from the laboratory. (Pitt and Lalor (2000) and Cowgill (1988) describe a steam-cleaning process which is thought to practically eliminate contamination from the surfaces. Steam cleaning will not be used because it may harm the roofing materials.) All panels will be decontaminated on the same day. Panels will be exposed to one rain event, as defined for this study, prior to the first sampling. Panels will not be rinsed between rain events.

Gutters

The Teflon®-lined HDPE gutters will be decontaminated initially using the following procedure. The gutters will be scrubbed 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 in accordance with Puget Sound Estuary Program protocols (PSEP, 1997). All stainless-steel sampling gear (56-liter stainless-steel runoff collection containers, mixing device and measuring device) 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). Prior to the first storm 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 water rinses will be discarded on 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.

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 <u>sample</u> taken at 9:15) ZIN-11-24-12-02 (field notebook would record <u>field split</u> taken at 9:25) ZIN -11-24-12-03 (field notebook would record <u>MS</u> taken at 9:35) ZIN -11-24-12-04 (field notebook would record <u>MSD</u> taken at 9:45)

Each sample that is couriered to the laboratory will have a sample tag 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 0.1 inch or 7.5 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. Calibrate the pH meter and the specific conductivity meter per SOPs EAP031 and EAP032, respectively (Ward, 2006 and 2011).
- 2. Label the sample bottles as described above.
- 3. Don a new set of nitrile gloves.
- 4. Remove the measuring device from the aluminum foil, touching it only with clean 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.
- 5. Remove the panel-specific tubing from the foil, setting it on the inside of the foil.
- 6. 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.
- 7. Remove the mixing device from the foil, using clean 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.
- 8. Continue mixing, while a second staff person removes the sample bottle cap with clean 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.
- 9. If dissolved metals will be sampled, follow SOP EAP029 (Ward, 2010). Fill the upper portion of the filtration apparatus provided by MEL with sample pumped from the container to the peristaltic pump into the filtration apparatus. Hand-pump the water through the filter. Pour the filtrate from the collection bottle into the pre-preserved sample bottle from the lab. Record the time at the end of the filtration process.
- 10. Fill each sample bottle to full, but not overflowing.
- 11. Recap the sample bottle tightly.
- 12. Complete the sample tag and attach the tag to the bottle.
- 13. If the sample bottle is glass, wrap it in bubble wrap and place it in the cooler.
- 14. Where split samples or QA samples are required, mix the stainless-steel runoff collection container while all samples have been obtained.
- 15. Fill a cup with sample from the stainless-steel container to measure pH using the protocols in EAP031 (Ward, 2006) and specific conductivity using the protocols in EAP032 (Ward 2011). Measure and record the pH and specific conductivity of the sample.
- 16. When all sampling for a panel has been completed, pour at least 1/2 liter of laboratoryprovided distilled water through the 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 the refrigeration unit.
- 3. Move all of the sampling equipment into the cleaning room and decontaminate the sampling equipment as described above. Obtain a composite sample of the final rinse from the stainless-steel containers, Teflon® and silastic tubing, mixing device, and measuring device. Ensure that you have at least 3 liters of rinsate for equipment rinse samples. Pump equipment rinse samples into the pre-cleaned laboratory sample bottles (one for each total metals, dissolved metals [if conducting dissolved metals], PAHs and phthalates, and PBDEs). 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 pickup by the MEL courier. Complete chain of custody forms.
- 4. Cover all decontaminated equipment in aluminum foil.
- 5. Create dissolved water blank samples by pouring laboratory-provided distilled deionized water into the sample bottle (one for each metals, PAHs and phthalates, and PBDEs). 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 pickup by the MEL courier. Complete chain of custody forms.

QA Samples and Blanks

Initial Blank Samples

The following blank samples will be obtained after decontaminating gutters and roof panels:

- Two initial distilled water blanks will be obtained after panels and gutters are decontaminated. One of these blanks will be prepared with laboratory-provided distilled deionized water. The second of these blanks will be prepared with distilled deionized water from the Ecology cleaning room at Headquarters facility. Staff will prepare blanks for total metals, PAH and phthalates, and PBDEs analyses for each of the two types of blanks.
- One initial equipment rinse blank will be obtained after the initial decontamination of the gutters. This blank will be a composite of a rinse from at least four gutters. This initial gutter equipment rinse will be analyzed for total metals, PAHs and phthalates, and PBDEs.

Rain Event Blank Samples

For each rain event sampled, the following blanks will be collected:

- One distilled water blank will be obtained for each sampling event and for total metals, PAH and phthalates, and PBDEs analyses, and dissolved metals if dissolved metals are sampled from the panels. The blank will be prepared by pouring laboratory-provided distilled deionized water directly into the sample bottles. For dissolved metals, dissolved water will be filtered and then poured into the pre-preserved laboratory bottle.
- One equipment rinse blank will be obtained as a composite of a rinse from decontaminated stainless-steel containers, tubing, measuring device, and mixing device. These will be obtained at the end of each sampling event. Equipment rinse blanks will be prepared for each of the parameters being sampled.

Rain Event Replicates and Splits

For each rain event sampled, the following replicates and splits will be collected:

- Samples will be obtained from each of the three asphalt shingle panels without algaeresistant (AR) copper granules. These samples will be obtained for all parameters in accordance with Tables 9 and 10, as appropriate. These are replicate samples.
- Three panels will be selected for split sampling from the remaining panels (i.e., not including the asphalt shingle without AR granules) where sufficient sample volume is available. Staff will rotate the split sample locations to ensure that over the course of the study splits are obtained from all of the panels. Split samples for all parameters do not need to be collected from a single panel. Split samples will be collected for all parameters sampled during a rain event.

Rain Event MS/MSD Samples

For each rain event sampled, the following MS/MSD samples will be collected:

• Three panels will be selected for MS/MSD sampling for each storm event. Panels will be selected where sufficient sample volume is available. Staff will rotate the MS/MSD sample locations to ensure that over the course of the study, MS/MSDs are obtained from all of the panels. MS/MSDs for all parameters do not need to be collected from a single panel. MS/MSD samples will be collected for all parameters sampled during a rain event.

Sample Packing and Shipping

Samples collected for laboratory analysis will be labeled, packed and shipped as follows:

- 1. Ensure the sample bottle is tagged 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 as listed in Table 12 of the QAPP ($\pm 2^{\circ}$ 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 outside lid of the ice chest. All samples will be in the control of the field crew until they are delivered to the storage cooler in the basement of the Ecology Building, which is under the control of Ecology.
- 6. Call the courier from MEL to let him know to transport the sample to the laboratory (at address below) on the next weekday.

Department of Ecology Manchester Environmental Laboratory 7411 Beach Drive East Port Orchard, WA 98366-8204 (360) 871-8800

7. After storing the samples in the cooler, call the laboratory project manager to report how many samples to expect and when to expect them to arrive.

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
- Matrix code (i.e., 10 for water)
- Source code (i.e., 17 for surface runoff)
- Date and time of sample collection (using a 24-hour clock)
- Analyses required
- Number of sample containers for each location
- Printed name and 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
- Name or reference number of the QAPP for the project
- SIC (charge code)
- Date results are needed (not more than 11 days after shipping)

The laboratory-signed, completed CoC will be scanned and emailed to Nancy Winters (<u>nwin461@ecy.wa.gov</u>) upon receipt by the laboratory and with the data package.

Field Notebook Records

All records of the project shall 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 conductivity 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 gage data logger
- Calculated rain depth (mm) downloaded from the rain gage data logger
- Depth and calculated volume of runoff collected from each roof type
- Measured pH and specific conductivity 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 to the courier pick up cooler

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 Nancy Winters at <u>nwin461@ecy.wa.gov</u>.

Re-Deployment

At the end of each rain event, the stainless-steel pans, 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 has elapsed since the preceding event with less than 0.1 inch of precipitation, 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 Ecology Headquarters facility and will not be used to maintain the area surrounding the pilot roofing panels. Normally this area of the Ecology Headquarters facility is allowed to grow until September of each year. Staff will monitor vegetation growth in the area surrounding the roofing panels monthly until mid-March and weekly thereafter. Staff will maintain the vegetation using hand-held equipment (such as 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.

				CH	AIN OF	CUSTO	DΥ									
Manchester Enviro	nmental Laboratory	,										Page:		of		_
			SIC: DST20				foronao #									
Project Name: Roofing Assessment		-	DSIZ	,		QAPP Re										
Send Results to: N						Email Add	iress: nw	/In461@ec	cy.wa.gov						-	
Phone: (360) 407-	/392															
Date of Sample Coll	ection:	1				Sample Lo	ocation:		i		1	Ī		1	1	
MEL Work Order #	Sample Number (Field Id)	Time	Matrix Code	Source Code	No of Containers	Total Metals As, Cd, Cu, Pb, Zn (200.8)	PAHs & Phthalates (8270 D)	PBDEs (8250)	SPLP (1312)	Other	Other	Other	Other	Other	Other	Field Notes
			10	17												
			10	17												
			10	17												
			10	17												
			10	17												
			10	17												
			10	17												
			10	17												
			10	17												
			10	17												
			10	17												
			10	17												
			10	17												
Relinquished by:		Received by:		Date/T	ime			Seal Id.			Condition of Seals	on S				Remarks:
Relinquished by:		Received by:		Date/T	ime			Seal Id.			Condition of Seals					Remarks:
Relinquished by: Received by: Date/Time				Seal Id.			Condition of Seals			Remarks:						
Relinquished by:		Received by:		Date/T	ime			Seal Id.			Condition of Seals					Remarks:

Appendix D. Estimated Analytical Costs

Table D-1. Cost estimates for sampling of pilot scale roofing panels

Samples for 7 rema	ining rain e	vents PAHs	
Roof Type	Metals	_	PBDEs
Glass (control)	2	2	2
Asphalt composite 6 types no			
algae control	3	3	0
Asphalt composite 6 types, wit	th		
algae control	1	1	0
Copper	1		
ТРО	1	1	1
PVC	1	1	1
EPDM	1	1	1
Zincalume	1		
Painted galv metal	1		
Wood shake/shingle	1		
Wood shake treated	1		
Concrete tile	1		
Built-up - oxidized granular ca	ρ		
sheet	1	1	
MBUR - granular SBS cap shee	t 1	1	
MBUR with granular APP cap		1	
sheet	1	1	
Count	18	12	5
Count	10	12	5
Total samples for Total metal	s for 1 stori	n	
Samples	18		
Field Reps	3		
MS/MSD	6		
Equip rinse blank/storm	1		
DI water blank/storm	1		
Tot	tal 29		
Dissolved metals samples for	1 storm ev	ent	
Samples	18		
Field Reps	3		
MS/MSD	6		
Filter blank	2		
Equip rinse blank/storm	1		
Tot	tal 30		
Total samples for PAHs and P	hthalates f	or 1 stoi	m
Samples	12		
Field Reps	3		
MS/MSD	6		
Equip rinse blank/storm	1		
DI water blank/storm	1		
Tot	tal 23		
Total samples for PBDEs for 1	storm		
Samples	5		
Field Reps	1		
MS/MSD	2		
Equip rinse blank/storm	- 1		
DI water blank/storm	1		
Tot	_		

Sample Costs - f				
	# of	cost/		
Parameter	samples	sample	Cost/storm	Parameter
Total Metals (5)	29	\$116	\$3,364	Total Metals (5)
PAHs +Phth	29	\$370	\$10,730	PAHs +Phth
PBDEs	29	\$177	\$5,133	PBDEs
Total for a single Storm Event			\$19,227	Total for a single
Dissolved Metals (3 events only)	90	\$138	\$12,443	
Initial equipment rinses (6) & 2 har	See b	elow	\$3,666	
	Total for	3 Storms	\$73,790	

Initial equipment rinses + hardness = 6*(\$116 + 370+117)+2*23.84 = \$3,666.

Sample Costs - remaining rain events						
	# of	cost/				
er	samples	sample	Cost/storm			
tals (5)	29	116	\$3,364			
nth	23	\$370	\$8,510			
	10	\$177	\$1,770			
a single Storm Even		\$13,644				
	Storms	\$95,508				

Table D-2. Cost Estimatles for Synthetic Precipitation Leaching Tests

	Repli	cates
		PAH +
Coupon Type	Metals	Phth
Galvanized steel	3	3
Galvalum®	3	3
Galvanized metal with sealant 1		
(Snow Seal)	3	3
Galvanized metal with sealant 2	3	3
Galvanized metal with sealant 3	3	3
Galvanized metal with sealant 4	3	3
Galvanized metal with sealant 5	3	3
Galvanized metal with sealant 6	3	3
Copper	3	3
Copper with sealant 1	3	3
Copper with sealant 2	3	3
Copper with sealant 3	3	3
SPLP blank	4	4
MS/MSD	8	8

Parameter	# of samples	analytical cost/sample	Total
SPLP Type Metals (As, Cd, Cu, Pb,Zn)	48	\$244	\$11,712
SPLP PAHs +Phth	48	\$370	\$17,760
Cost for three replicates of each coupon			\$29,472

Total samples for metals	48
Total samples for PAHs and Phthalates	48

Appendix E. Modifications to EPA Method 1312, Synthetic Precipitation Leaching Procedure

The Synthetic Precipitation Leaching Procedure (SPLP) methodology will be modified for the Roofing Assessment Project as follows:

- 1. Roof samples will remain whole, not ground up.
- 2. Roof samples will be used as solid square pieces and will measure approximately 1.0 inch by 1.0 inch on a side.
- 3. Each dimension of each roofing sample will be measured to the nearest 1.0 mm and measurements recorded.
- 4. The weight of each roofing sample will be measured to the nearest 0.1 mg and recorded.
- 5. Exactly 1.7 liters of synthetic precipitation will be added to each beaker for extraction. This represents the volume of precipitation landing on two square inches of surface area in one year in Olympia, Washington. (51 inches of rain falling on 2 square inches of roofing would generate 0.059 cubic feet of volume, which, when multiplied by 7.48 gallons/cubic foot and 3.785 liters/gallon, yields 1.7 liters.)
- 6. The remainder of the EPA method will be followed as written.

Appendix F. Glossary, Acronyms and Abbreviations

Glossary

Batch: Laboratory samples that are analyzed in the same group, usually 20 samples or less.

Distilled Water Blank: Distilled deionized water that is provided by the laboratory and which is sampled and analyzed to determine whether contaminants of concern are present.

Equipment Rinse: Distilled deionized water that is provided by the laboratory, used as a final rinse after equipment decontamination. This water is sampled and analyzed to determine whether contaminants of concern are present.

Field Split: Samples of runoff obtained from a single collection container. Samples will be obtained during mixing.

Field Replicate: Samples of runoff obtained from roofing panels constructed of the same type of roofing materials and installed implementing the same procedures.

Median: A mathematical expression of the middle value of a set of values, above which 50% of the data exists and below which 50% of the data exists.

Parameter: A physical chemical or biological property whose value determines environmental characteristics or behavior.

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

Rain event: A rain event is defined by four factors: the minimum and maximum depth of rainfall, the length of an event, and the antecedent dry condition. For this study, the minimum rainfall is one required to generate 7.5 liters (0.1 inch or 2.54 mm assuming 100 percent runoff). The maximum rain event to be monitored can generate no more than 56 liters (15 gallons) of runoff (0.75-inch rain event). A rain event will not exceed 24 hours. The minimum antecedent dry period between rain events is defined as 6 hours of less than 0.1 inch of precipitation.

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

10th percentile: A statistical number obtained from a distribution of a data set, above which 90% of the data exists and below which 10% of the data exists.

50th percentile: A statistical number obtained from a distribution of a data set, above which 50% of the data exists and below which 50% of the data exists; also termed the median value.

90th percentile: A statistical number obtained from a distribution of a data set, above which 10% of the data exists and below which 90% of the data exists.

Acronyms and Abbreviations

APP	Atactic polypropylene roofing
AR	Algae-resistant
BMS	Building Materials Specialist
BUR	Built-up roof
CCA	Chromated-copper-arsenate
DBP	Di-n-butyl phthalate (DBP)
DEHP	Bis (2-ethylhexyl) phthalate
DIDP	Diisodecyl phthalate
DINP	Diisononyl phthalate
EAP	Environmental Assessment Program
Ecology	Washington State Department of Ecology
e.g.	For example
EIM	Environmental Information Management database
et al.	And others
EPA	U.S. Environmental Protection Agency
EPDM	Ethylene propylene diene monomer
HDPE	High density polyethylene
HVAC	Heating, ventilation, and air conditioning
i.e.	In other words
MDL	Method detection limit
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
MS	Matrix spike
MSD	Matrix spike duplicate
NADP	National Atmospheric Deposition Program
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyls
PVC	Polyvinyl chloride
QA	Quality assurance
RL	Reporting limit
RPD	Relative percent difference
RTF	Roofing Task Force
SPLP	Synthetic Precipitation Leaching Procedure
SBS	Styrene butadiene styrene
SOP	Standard Operating Procedure
TPO	Thermoplastic polyolefin roofing
-	r ····· r· /······

XRF X-ray fluorescence

Units of Measurement

ft	feet
g	gram, a unit of mass
kg	kilograms, a unit of mass equal to 1,000 grams
m	meter
mg/L	milligrams per liter (parts per million)
mL	milliliters
mm	millimeter
mm/hr	millimeters per hour
ug/L	micrograms per liter (parts per billion)