Roofing Materials Assessment

Investigation of Toxic Chemicals in Roof Runoff

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Photo provided courtesy of Russ McMillan, Department of Ecology, Toxics Cleanup Program.

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Abstract

From February through April 2013, the Washington State Department of Ecology collected runoff from 18 constructed roofing panels following 10 rain events for contaminant analysis. Analysis of the runoff included total and dissolved metals (arsenic, cadmium, copper, lead, and zinc) and organic compounds [polycyclic aromatic hydrocarbons (PAHs), phthalates, and polybrominated diphenyl ethers (PBDEs)].

Ecology identified significantly higher concentrations of three metals in runoff from several roofing panels when compared to the glass control panels. Most notably, concentrations of total arsenic, copper, and zinc were significantly higher in the following roofing panels than in the glass control panels: treated cedar shakes (arsenic and copper), copper (copper), Zincalume® (zinc), and EPDM (zinc).

- Arsenic levels in runoff from the treated wood shake panel ranged from 692 to 4,690 ug/L, and copper levels ranged from 601 to 3,190 ug/L.
- Copper levels in runoff from the copper panel ranged from 1,035 to 3,380 ug/L.
- Zinc levels in runoff from the Zincalume® panel ranged from 38 to 322 ug/L
- Zinc levels in runoff from the EPDM panel ranged from 44 to 313 ug/L.

Ecology compared concentrations of metals in runoff with concentrations used to estimate releases to the Puget Sound basin in Ecology's 2011 study. With two exceptions, concentrations ranged from two-fold to two orders of magnitude higher in Ecology's 2011 study than were found in this 2013 study. However, runoff concentrations used to estimate releases to the Puget Sound basin in 2011 were based on roofing systems, rather than roofing materials alone.

The new roofing materials in this study did not leach PAHs or PBDEs to the runoff. With one exception (treated cedar shake panel), the new roofing materials evaluated did not leach phthalates.

Runoff from the roofing panels from 10 additional rain events were sampled in late 2013 and early 2014. Those results will be described in a separate report.

Leaching analysis of copper and galvanized steel coupons (samples), with and without post-manufactured applied coatings, indicated that the coatings reduced the copper and zinc leaching, despite problems with the leaching methodology.

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Acknowledgements

Funding
National Estuary Program (NEP) funding for this project was provided by the U.S. Environmental Protection Agency (EPA). This study was also funded by the Pollution Prevention Unit of the Washington State Department of Ecology's (Ecology's) Hazardous Waste and Toxics Reduction Program.

Roofing Panel Donations
Ecology wishes to thank the following manufacturers and organizations who graciously donated the roofing materials for the panels:

Companies	***Roofing Materials Donated***
CertainTeed, GAF, IKO, Malarkey, Owens Corning, and PABCO	Asphalt shingles
Malarkey Roofing	Built-up and modified built-up roofing materials
Copper Development Association	Copper
SPRI	TPO, EPDM, and PVC
Cedar Shake and Shingle Bureau	Treated cedar shakes and untreated cedar shingles
Steelscape	Zincalume® and painted galvanized roofing
Tile Roofing Institute	Concrete tile

Construction
This project could not have succeeded without the work of Brian Pickering and Mike McKay from Ecology's Operations Center. They were instrumental in developing the design of the panel structures, gutters, mixing and measuring devices, as well as collection container boxes and stands that prevented rain from entering the sample containers. They spent hundreds of hours constructing the panel assemblages, transporting them, and ensuring contractors had access to the site during the week of roof panel installation.

Ecology also thanks the following firms and individuals who installed the roofing panels:

Name	***Representing***
Jerry Iselin	Metal Roof Specialist
Joe Russo	Malarkey Roofing
Sid Dinwiddie and staff	PABCO
Marty Obando	(Individual)
Don Guthrie and staff	Wayne's Roofing
Douglas French	Tin Man
Wayne Seale and associate	Copper Development Association
Peter Parmeter	Cedar Shake and Shingle Bureau
Paul Riesebieter	Johns Manville
Kevin Kelly	Durolast
Renee Ramey	Steelscape
Rick Olsen	Tile Roofing Institute

Sealants
Steve Heinje of United Coatings/Quest CP served an instrumental role in educating us about coatings and their properties and also helping select coatings for the coupons (samples) exposed to the SPLP analysis. Steve helped us make thoughtful and informed decisions in selecting coatings. We are also grateful to the following companies who donated coating material:

- Ames Research Laboratories
- Quest Coatings
- The Roof Doctor
- Sherwin Williams

Sampling and Other Assistance
This project could not have been successfully completed without those who helped with the sampling. All were with Ecology when we sampled, except for Lisa Rozmyn who is with the Washington State University Stormwater Center.

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- Tom Gries
- Alli Kingfisher
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- Leon Weiks
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- Bob Bergquist
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- Don Fisher
- Michael Friese
- Steve Fry
- Dennis Lorton
- Brandi Lubliner
- Evan Newell
- Valerie Partridge
- Chuck Springer
- Chuck Wilkowski

Finally, we wish to thank the members of the Roofing Task Force (RTF). The Executive Summary describes the activities of this group.

Name	***Representing***
Jeff Jacobs	3M
Frank Klink	3M
Wayne Neumann	3M
Edward Karpe	Akzo Nobel Coatings Inc /Metal Alliance
Bob Gruber	Arch Wood Protection, Inc.
Mike Fischer	Asphalt Roofing Manufacturers Association (ARMA)
John Ferraro	ARMA
Troy Gamba	Boeing
John White	Boeing
Dan Welch	Bundle Design Studio
Lynne Christiansen	Cedar Shake and Shingle Bureau
Steve Johnston	CertainTeed
Dennis Wilson	CertainTeed
Kevin Kelley	Chemical Fabrics and Films Association (CFFA)/Duro-Last Roofing
Joseph Gorsuch	Copper Development Association Inc.
Wayne Seale	Copper Development Association Inc.
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Mike Hubbard	Firestone and Single Ply Roofing Institute (SPRI)
Heather Trim	Futurewise
Shawn Stanley	IB Roof Systems
Eric Van Genderen	International Zinc Association
David Batts	King County Natural Resources
Greg Malarke	Malarkey Roofing
Joe Russo	Malarkey Roofing
Mike Tuel	Malarkey Roofing
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Mark Graham	National Roofing Contractors Association (NRCA)
Jason Wilen	National Roofing Contractors Association (NRCA)
Howard Thurston	Northwest EcoBuilding Guild
Chuck Shaw	Osmose, Inc.
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Rick Olson	Tile Roofing Institute (TRI)
Stephen Heinje	United Coatings/Quest CP
Bruce Wishart	Washington Environmental Council – People for Puget Sound
Scott Tobiason	Windward Environmental
Lisa Rozmyn	Washington Stormwater Center
Brian Penttila	Pacific Northwest Pollution Prevention Resource Center

Executive Summary

During the Puget Sound Toxic Chemical Assessment (2010 and 2007-2011), the Washington State Department of Ecology (Ecology) applied literature values to estimate contaminant releases from various sources to the Puget Sound basin (Ecology, 2011a and b). The Puget Sound basin is comprised of all the freshwater bodies within the 12-county watershed that ultimately flow into the waters of Puget Sound and the Strait of Juan de Fuca.

Ecology estimated that approximately 88% of the zinc, 60% of the cadmium, 20% of the arsenic, and 10% of the copper released within the Puget Sound basin were associated with roof runoff (Ecology, 2011a and b). Regional data were lacking in this assessment, and most of the literature values used by Ecology came from complete roofing systems. Ecology felt that more data were needed to assess roofing as a source of contaminants. To this end, the present study was conducted to determine whether one element of roofing systems, roofing materials, contribute to releases of toxic chemicals.

This 2013 study had two major components:

- **The Pilot-Scale Roofing Assessment** focused 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 gutters and downspouts, HVAC systems, flashings, exposed fasteners, and post-manufactured treatments, to name a few. This pilot study was the first step in a systematic approach to assessing toxic chemical releases from roofing systems. The study evaluated runoff from the most commonly used roofing materials in the Puget Sound basin, and roofing materials recommended by the Roofing Task Force. Only new roofing materials (i.e., un-aged materials provided and installed by the manufacturers and their contractors at the beginning of the study) were used.
- **The Synthetic Precipitation Leaching Procedure (SPLP)** focused on determining the effectiveness of the post-manufacturer applied coatings at reducing metals leaching. Ecology assessed coupons (samples) with and without post-manufacturer applied coatings to determine whether coatings would leach organic contaminants to the synthetic precipitation, thereby exchanging release of one toxic compound for another toxic compound and not necessarily achieving environmental benefit. Ecology also conducted the SPLP coupon assessment to identify a potentially more cost-effective method to simulate contaminant concentrations in rain runoff for future studies.

The methods and findings of these two components of the study are presented separately in this Executive Summary but are integrated in the body of the report.

Pilot-Scale Roofing Assessment

In 2012, Ecology convened a Roofing Task Force (RTF) of manufacturers, contractors, and other stakeholders to provide input to the design of this study. RTF members were solicited through associations and roofing manufacturers. As the project progressed, associations identified other potential members who ultimately joined the group.

In discussing design options, the RTF favored a pilot-scale study, with the hope that the roofing panels could be used subsequently to assess the impacts of other factors, including roof aging. The RTF also recommended and provided the roofing materials assessed. Their comments on the draft Quality Assurance (QA) Project Plan were addressed in the final plan, describing the detail of the study.

Ecology also solicited RTF comments on the draft report, incorporating changes to produce the final report. The comments and Ecology's responses are published as a supplement to this final report.

Methods

Manufacturers and associations donated and installed the roofing materials on 18 4-by-8-foot, pilot-scale roof panels at Ecology Headquarters in Lacey, Washington. The panels represented 14 types of roofing materials, two replicates of the asphalt shingle roofing material, and two glass control panels. The roofing materials evaluated are listed in Table ES-1. Because manufacturers selected the specific products to be evaluated, the roofing materials assessed do not necessarily represent a random selection of materials available.

Table ES-1. Panel materials and identification codes.

Steep-Slope Panels	**ID Code**
Asphalt shingle – composite of 6 types of shingles with algae resistant (AR) copper-containing granules	ARR
Asphalt shingle – composite of 6 types of shingles without algal resistant (AR) granules*	AS-1, AS-2, AS-3
Copper	CPR
Concrete tile	CTI
Manufacturer-painted galvanized steel, painted with silicone-modified polyester paint	PAZ
Manufacturer-treated wood shake	TWO
Wood shingle	WOS
Frosted glass (control) at steep slope	GST
Low-Slope Panels	
Modified built-up roof with Atactic polypropylene (APP) granulated cap sheet	BUA
Built-up roof with oxidized asphalt granulated cap sheet	BUR
Modified built-up roof with styrene butadiene styrene (SBS) granulated cap sheet	BUS
Ethylene propylene diene monomer (EPDM)	EPD
Polyvinyl chloride (PVC)	PVC
Thermoplastic polyolefin (TPO)	TPO
Zincalume® (a trade name for Galvalume)	ZIN
Frosted glass (control) at low slope	GLO

* Results of these replicates were systematically averaged in this study and denoted as AS^{A}.

Steep-slope roofing panels were installed at 26.5^o angle from the horizontal, typical of residential roof slopes. The low-slope roofing panels were installed at 1.2^o (known as ¼:12 in the industry), typical of commercial roofs. All panels faced south southwest, the prevailing wind direction.

Ecology staff collected runoff from 10 rain events from February through April 2013. Precipitation landing on a panel flowed into Teflon®-lined removable gutter and into 56-liter stainless-steel pot. Samples were obtained from the stainless-steel containers and shipped to the laboratory for analysis. The runoff samples collected from each rain event represented an integration of the water that ran off during the entire monitored event.

During the first three of the 10 rain events, all of the following parameters were analyzed:

- Total metals (arsenic, cadmium, copper, lead, and zinc)
- Dissolved metals (arsenic, cadmium, copper, lead, and zinc)
- Polycyclic aromatic hydrocarbons (PAHs) and phthalates
- Polybrominated diphenyl ethers (PBDEs) potentially used as flame retardants

For the remaining seven rain events, total metals were analyzed in the runoff from every panel. PAHs and phthalates were analyzed in the runoff from single-ply, asphalt-based, and glass control panels; and PBDEs were analyzed in the runoff from single-ply and glass control panels. Ecology also recorded field parameters including pH, specific conductance, temperature, and volume of the runoff.

Findings

Based on the data collected, the roofing materials tested released low concentrations of total metals with the following exceptions:

- The treated wood shake panel (TWO) was treated with chromated copper arsenate (CCA) and met the substantive portions of the best management practices (BMPs) prescribed by the Western Wood Preservers Institute (WWPI). This panel released concentrations of arsenic (692 to 4,690 ug/L) and copper (601 to 3,190 ug/L). These concentrations were significantly higher than those from the glass control panel. The treated wood shake panel also released low, but significantly higher, concentrations of cadmium than the glass control panel.

- The new PVC panel released concentrations of arsenic in the runoff that ranged from 22 to 117 ug/L and were significantly higher than levels from the glass control panel. Arsenic likely serves as a biocide in the PVC matrix.

- The copper panel (CPR) released concentrations of copper that ranged between 1,035 and 3,380 ug/L and were significantly higher than the glass control panel.

- The asphalt shingle panel with AR (AAR) and the asphalt shingle panels without AR (AS^A) concentrations of copper were also significantly higher than the glass control panel, although these concentrations were one to two orders of magnitude lower than released by the copper panel.

- The Zincalume® (ZIN) and EPDM panels released concentrations of zinc significantly higher than the low-slope glass control panel. Zinc represents one of two metals in the Zincalume® alloy. Zinc is used as a catalyst in the manufacturing of EPDM.

- The painted galvanized metal (PAZ), treated wood shake (TWO), wood shingle (WOS), and asphalt shingle with AR (AAR) panels released concentrations of zinc that were significantly higher than the glass control panel. However, zinc in the runoff from these panels was up to an order of magnitude lower than zinc released from the ZIN and EPDM panels.

PAHs in runoff from the new roofing panels were low and not distinguishable from PAHs in runoff from the glass control panels, even in those roofs which have asphalt components (such as asphalt shingles and built-up roofing). PBDEs were also low in the runoff from the new roofing panels tested.

Phthalates in runoff from the new roofing panels were low. For all but one type of roofing material, phthalates concentrations were not distinguishable from levels from the glass control panels. The only exception, the treated wood shake panel (TWO), had detectable concentrations of phthalates including bis (2-ethyl hexyl) phthalate. These may have originated from vacuum pump oil used during the pressure treatment process.

Comparisons of concentrations of metals in roof runoff in this study with the concentrations used to estimate releases in the Puget Sound Toxics Assessment (2011a) revealed that for every metal and every roofing material evaluated (except copper in runoff from a copper panel and arsenic in runoff from the asphalt shingle panel with AR), concentrations in this study ranged from two-fold to two orders of magnitude lower. However, runoff concentrations used to estimate releases in the Puget Sound Toxics Assessment were based predominantly on full-scale roofing systems rather than roofing materials alone.

Recommendations

The results collected in this initial investigation did not provide Ecology with a long enough period of record to have confidence in making decisions about future actions related to assessing roofing materials or whether source control actions are needed for the materials tested. Ecology determined that a robust baseline from a single location over a one-year period would better serve the on-going studies of these roofing panels. To that end, Ecology continued sampling runoff from the panels for another 10 rain events in the fall and winter of 2013/2014. The additional data collection will provide greater statistical power in discerning differences between roofing materials and changes over time.

Given that even the highest zinc concentrations in runoff from the Zincalume® (ZIN) and EPDM panels were an order of magnitude lower than the mean concentrations used by Ecology to assess sources of contaminants in Puget Sound from roofing systems (Ecology, 2011a), Ecology recommends that other components of roofing systems (e.g., flashings, downspouts, gutters, HVAC) be evaluated to assess releases of metals to stormwater runoff. Additionally Ecology recommends that other factors affecting contaminant release be investigated, such as roofing maintenance and repair products, as well as the fate and transport of the contaminants once released into the environment.

Concentrations of total arsenic, copper, lead, and zinc were consistently measured in runoff from all of the new roofing materials evaluated. As roofing materials age, the concentrations of metals released may change over the life of a roof. Ecology recommends that the impacts of aging on metals release continue to be monitored over the lifespan of the materials. A longer-term assessment would help to determine whether contaminants leach in greater or lesser amounts with age. Future investigations should continue to assess not only total metals concentrations but also PAHs, phthalates, and PBDEs at lower frequencies.

In February 2014, Ecology moved the roofing panels to the Washington Stormwater Center in Puyallup, Washington for continued research, as funding becomes available.

Synthetic Precipitation Leaching Procedure (SPLP)

Methods

Ecology assessed one-inch coupons (samples) of galvanized zinc and copper with and without post-manufacturer applied coatings. Coatings were selected for evaluation with the assistance of the Roofing Task Force member with coatings experience. These represented elastomeric, acrylic, and silicon, and asphaltic-based coatings. Ecology staff hand-applied two coats of each product to all surfaces of the galvanized zinc coupons, while the manufacturer applied the coatings to the copper coupons. Table ES-2 lists the coupon materials and coatings evaluated.

Table ES-2. Coupon materials and coating types.

Materials and Sealants
Zincalume®, uncoated
Galvanized steel, uncoated (galvanized steel was not assessed in this pilot study)
Galvanized steel coated with Ames Research Laboratory Inc. Snow Seal™
Galvanized steel coated with Sherwin Williams SHER-CRYL™ HPA High Performance Acrylic Semi-Gloss Coating
Galvanized steel coated with Sherwin Williams UNIFLEX® Elastomeric Roof Coating
Galvanized steel coated with Coatings & Foam Solutions Poly-Sil 2500 High Solids
Galvanized steel coated with Karnak® Fibered Aluminum Asphalt Coating 98AF
Galvanized steel coated with Quest Construction Products Elastuff™ 101
Copper, uncoated
Copper coated with Syncrylac®
Copper coated with PPG Architectural Finishes Coraflon® ADS Intermix

Replicate coupons of each type were exposed to SPLP leachate (pH 5.0) designed to simulate slightly acidic rain for an 18-hour to 20-hour period of tumbling. The leachate was analyzed for total metals (arsenic, cadmium, copper, lead, and zinc), PAHs, and phthalates. For one coating on galvanized steel, three replicate coupons were exposed to the procedure and analyzed for PBDEs, as PBDEs were suspected chemical constituents used in the production of this coating.

Because no galvanized steel roofing panel was assessed as part of the pilot-scale roofing assessment, Ecology also compared leaching from a galvanized steel coupon to a Zincalume® coupon.

Findings

The following findings can be drawn from the modified SPLP analysis of galvanized steel and copper coupons with and without various coatings:

- While the coatings were damaged in the SPLP tumbling procedure, all coatings of the metal coupons reduced the concentrations of zinc or copper released from the galvanized steel and copper coupons, respectively.
- Coatings reduced the zinc concentrations in the leachate between 47% and 91%. Generally the thicker the coating, the greater the zinc reduction realized.
- Low levels of PAHs were detected leaching from the coatings, but these were at concentrations generally less than 0.1 ug/L. The Karnak Fibered Aluminum 98AF coating released the greatest numbers of PAHs, while the Elastuff™ 101 released the highest concentration of total PAHs.
- One phthalate and one PBDEs congener were detected leaching from the Elastuff™ 101 coating, but in only one of the three coupons. Based on a single detection of each of these two compounds, Ecology did not conclude that Elastuff™ 101 releases these compounds.
- Ecology compared the release of zinc and copper from the Zincalume® (ZIN) and copper roofing panels (CPR) exposed to precipitation to that of the uncoated Zincalume® and copper coupons exposed to the SPLP test. For the Zincalume® and copper panels, these calculations resulted in releases of 0.54 ug zinc/yr cm^2 and 7.09 ug copper/yr cm^2, respectively. The metals leached from the uncoated Zincalume® and copper coupons in the SPLP leachate resulted in much higher values: 42.1 ug zinc/yr cm^2 and 43.1 ug copper/yr cm^2, respectively. These results suggest that the SPLP test, as used in this study, should not be used to simulate runoff from roofing materials.

Recommendations

Ecology's intent in conducting the SPLP portion of the study was to determine the effectiveness of the coatings at reducing metals leaching to simulated precipitation. Ecology also intended to determine whether coatings could leach organic contaminants, thereby exchanging release of one toxic compound for another toxic compound, not achieving a net environmental benefit. More work is needed in this area in at least two arenas:

- To better simulate precipitation, the SPLP methodology should be substantially modified. A custom SPLP-like method should be developed to better mimic precipitation runoff. This would reduce costs of larger-scale testing.

- Before recommending any of the coatings assessed in this study, the coatings should undergo a thorough alternatives assessment emphasizing hazard assessment, using the GreenScreen™ methodology and including all pertinent life-cycle impacts.

Introduction

Between 2007 and 2011, the Washington State Department of Ecology (Ecology) conducted assessments of contaminant releases from various sources in the Puget Sound basin (Ecology, 2011a and b). The Puget Sound basin is comprised of all the freshwater bodies within the 12-county watershed that ultimately flow into the waters of Puget Sound and the Strait of Juan de Fuca.

The reports estimated that approximately 88% of the zinc, 60% of the cadmium, 20% of the arsenic, and 10% of the copper released within the Puget Sound basin were associated with roof runoff (Ecology, 2011a and b). The report also noted that polycyclic aromatic hydrocarbons (PAHs) and phthalates may also be released from roofing systems to the Puget Sound basin. However, the assessment used literature values from various locations across the U.S. and the world to represent contaminant concentrations in Puget Sound. A number of regional factors such as precipitation volume, duration, and intensity, pH, and roofing materials used in the basin could have a significant impact on the release of contaminants from roofing materials.

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

Need for a Puget Sound Basin Roofing Assessment

A recent assessment of the human-caused (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 a comparatively minor source of phthalates and PAHs (Ecology, 2011a). Ecology obtained information on chemical concentrations used to derive these estimates primarily from the published literature.

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 less acidic than the pH values measured by Clark in the most extensive studies of roofing materials in the U.S. which controlled for atmospheric deposition (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), or flexible polyvinyl chloride (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) and modified BURs installed using either coal tar or asphalt, or asphalt shingle roofs. Modified BURs are roof systems composed of two or three polymer-modified membrane layers adhered using hot asphalt, cold adhesive, or by torching down the membrane. The polymer modified membranes are made from mixtures of asphalt and polymer (e.g., atactic polypropylene [APP] or styrene butadiene styrene [SBS]) coated on glass or polymer fiber mat. Runoff from these materials has not been assessed for many of the chemicals that could potentially leach from them.

A Puget Sound study would help to determine whether the contaminant sources attributed to roofing in the Puget Sound Toxics Assessment (Ecology, 2011a) are applicable to the roofing materials and conditions in the Puget Sound region. 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 amounts 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.

Literature Review

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 or other inorganic compounds, 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 may have the potential to release arsenic, cadmium, chromium, copper, lead, nickel, and zinc; phthalates; biocides, nonylphenols, and thiocyanate (Björklund, 2011). The pollutants carried 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 reportedly contribute up to 80% of the cadmium, lead, and zinc to wet weather flows of Paris (Gromaire et al., 2001).

Metal Roofs

Metal roofs are often constructed from thin sheets of zinc, galvanized metal, or copper. Rolled zinc roofs are more common in Europe, while galvanized metal roofs are common in the U.S. 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 the higher concentrations of the first flush) 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 from 1.8 to 3.9 mg/L for new copper roofing and from 2.4 to 5.4 mg/L for 30-year-old copper roofing.

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., 2002), with a median of the literature values reviewed of 2,400 ug/L. See Table 1 for comparisons.

Swiss authors reported that the rate of release (g/m^2-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 1 summarizes literature values reported for total metals concentrations.

The literature provides a variety of results (some representing the first-flush concentrations, others representing steady-state or post-first-flush conditions). Others integrated the sample results and presented them as event mean concentrations. To be as comparable as possible, the total metals concentrations listed in Table 1 reflect total metals measured in post-first-flush runoff or event mean or median concentrations categorized by roofing material. Where concentrations are negative, aerial deposition was greater than the concentrations in the runoff. By contrast, the Puget Sound Toxics Assessment (Ecology, 2011a) used the means of values reported throughout the literature. Resulting concentrations were then used for calculating releases within the Puget Sound basin.

The levels of metals leached by precipitation from roofing strongly depend on the composition of the roofing. However, the metals composition of the roofing material may not affect the concentrations of those metals in the runoff in the anticipated fashion. Brunk et al. (2009) noted that metal alloys impacted the runoff in unexpected ways. They noted that although the bulk composition of zinc and copper in bronze was 15% zinc and 85% copper, the runoff composition from this 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 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 metal sheets.

The availability of metals to leach from roofing also strongly depends on the composition of coatings (i.e., sealants) that may be applied to the roof surface. For example, phosphated and chromated coatings were demonstrated to reduce the concentrations of zinc substantially (Table 1). Aluminum-zinc alloy products such as Galvalume® or Galfan® resulted in lower zinc concentrations in the runoff as well (Clark, 2010; Mendez et al., 2010; Heijerick et al., 2002). Tobiason's (2004) Galvalume® roof is comprised of an aluminum zinc alloy and released substantially lower concentrations of zinc than pure galvanized metal. Table 1 indicates that releases from Galvalume® roofs generally resulted in substantially lower concentrations than from galvanized metal roofs.

Table 1. Concentrations of total metals (in ug/L) measured in roof runoff from studies by roof type.
Total metals concentrations represent post-first-flush means or medians or event mean concentrations.

Roof Type	Location	Arsenic	Cadmium	Copper	Lead	Zinc	pH of 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 zinc 40 years old	Paris, France		3.2	2.2	30.2	7,080		Robert-Saint et al. (2009)
Galvanized Steel Roofs								
Metal - weathered and maybe coated with aluminum paint	Washington			4	8	1,040		Good (1993)
General galvanized steel (hot dipped)	Sweden					5,500	6.3	Heijerick et al. (2002)
Galvanized iron	Malaysia				199	423	6.6	Yaziz et al. (1989)
Galvanized iron - galvanized gutter (wet & dry deposition subtracted from results)	Texas	NM	NM	<1	<1	8,134	5.5	Chang et al. (2004)
Steel with zinc coating	Paris, France		ND	ND	0.3	3,081		Robert-Saint et al. (2009)
Galvalume® and Coated Steel Roofs								
Galvalume® (55% aluminum, zinc coated steel)	Washington			22		2,890		Tobiason (2004)
Galvalume® (55% aluminum, zinc coated steel)	Pennsylvania	-0.3	1.3	-59	2.1	24.8	4.3	Clark (2010)
Galvalume®	Texas	<0.29	<0.10	2.2	0.7	118	6	Mendez et al. (2010)
Galvalume®	Sweden					1,600	5.8	Heijerick et al. (2002)
Galfan® (aluminum coated)	Sweden					1,600	5.9	Heijerick et al. (2002)
Galfan® + total organic carbon top coating	Sweden					700	5.9	Heijerick et al. (2002)
Zinc Anthra (phosphated zinc product)	Sweden					2,300	6	Heijerick et al. (2002)

Roof Type	**Location**	**Arsenic**	**Cadmium**	**Copper**	**Lead**	**Zinc**	**pH of rain**	**Author**
Anthra metal with zinc $(PO_4)_2$ coating	Paris, France		ND	0.1	1.1	3,597		Robert-Saint et al. (2009)
Prepainted Zincalume®	Washington			1.3		146		Herrera (2011)
Zinc Quartz (phosphated zinc product)	Sweden					2,500	6	Heijerick et al. (2002)
Galvanized steel + chromium seal	Sweden					2,400	6	Heijerick et al. (2002)
Galvanized steel + total organic carbon	Sweden					1,200	5.7	Heijerick et al. (2002)
Prepainted galvanized steel	Sweden					160	5.4	Heijerick et al. (2002)
Painted steel	Sweden					2,100		Persson & Kucera (2001)
Prepainted galvanized steel. Stainless with zinc coating and polyester top coat	Paris, France		ND	2.9	0.5	31		Robert-Saint et al. (2009)
Other Metal Roofs								
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	-0.4	0.2	-31	6.1	5,751	4.3	Clark (2010)
Aluminum galvanized gutter (wet & dry deposition subtracted from results)	Texas			1	<1	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)

Roof Type	Location	Arsenic	Cadmium	Copper	Lead	Zinc	pH of rain	Author
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)
Tile Roofs								
Concrete tile	Texas	0.42	<0.10	5.3	1.3	91	6	Mendez et al. (2010)
Concrete tile	Malaysia				197	94	6.9	Yaziz et al. (1989)
Concrete tile	Sweden			<20	3.5	25		Persson & Kucera (2001)
Clay tile (old copper gutters)	Switzerland			71	13	10		Zobrist et al. (2000)
Clay tile (wet deposition subtracted from results)	Texas				<1	320		Chang & Crowley (1993)
Ceramic tile	Nigeria		550		1,110	850		Ayenimo et al. (2006)
Shingle Roofs								
Asphalt shingle with algae resistance (AR)	Pennsylvania	0.3	ND	ND	ND	ND	4.3	Clark (2010)
Asphalt shingle - galvanized gutter (wet & dry deposition subtracted from results)	Texas			-3	<1	774	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. (2010)
Asphalt - residential						149.0		Bannerman et al. (1993)
Asphalt - residential	Michigan & Wisconsin			0.7	10	318		Steuer et al. (1997)
Synthetic Roofs								
Corrugated PVC	Pennsylvania	0.1	-0.3	-0.2	0.1		4.3	Clark (2010)
Rubber roofing	Pennsylvania	-0.3	1.9	-26	1.3	94	4.3	Clark (2010)
Ondura®	Pennsylvania	-0.1	-0.1	-64	0.2	115	4.3	Clark (2010)
Cool	Texas	<0.29	<0.10	1.3	0.6	46	6	Mendez et al. (2010)
Polyester (new copper gutters)	Switzerland			217	4.9	27		Zobrist et al. (2000)

Roof Type	Location	Arsenic	Cadmium	Copper	Lead	Zinc	pH of rain	Author
Built-Up and Other Institutional Roofs								
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		Zobrist et al. (2000)
Wood and Treated Wood Roofs								
Wood shingle - galvanized gutter (wet & dry deposition subtracted from results)	Texas			1	<1	9,632	5.5	Chang et al. (2004)
Cedar shakes	Pennsylvania	-0.3	-0.4	-29	0.8	201	4.3	Clark (2010)
Untreated southern pine decking	Florida	2						Khan et al. (2006)
Untreated plywood	Pennsylvania	-0.3	0.1	-55	1.6	ND	4.3	Clark (2010)
CCA treated southern pine decking	Florida	600					4.5	Khan et al. (2006)
Pressure treated/water sealed wood	Pennsylvania	4.2	0.03	1,867	ND	890	4.3	Clark (2010)
Pressure treated wood	Pennsylvania	1.3	0.1	1,691	-0.4	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)

ND: not detected
NM: not measured
CCA: chromated copper arsenate

Pre-painted zinc surfaces (manufacturer-painted) can result in concentrations that are two orders of magnitude below those from raw galvanized surfaces (Table 1). Robert-Sainte et al. (2009) assessed a galvanized surface coated with a polyester paint, while Heijerick et al. (2002) assessed pre-painted galvanized steel.

Post-manufacturer painting has had mixed results. Taylor (2004) found an 81 to 87% reduction of total zinc in synthetic runoff by painting a previously installed galvanized metal roof. Tobiason et al. (2006) found general reductions of approximately 37% in the total zinc released from a Galvalume® surface after painting and subsequent removal of gutter sediments. On the other hand, 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. The authors suggested that this was likely a function of the composition of the zinc-containing paint.

Age of Metal Roofing Materials

The literature contains conflicting reports about the relationship between the age of the roofing material and the amount of metal leached from it during precipitation events. 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 1). 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. (2008) found greater zinc loading associated with older zinc roofing.

Odnevall Wallinder et al. (1998) conducted an extensive study of corrosion rates of 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, they reported that once the patina had aged, the dissolution and runoff of the metal were in steady-state with the metals in the patina.

Dissolved Metals from Metal Roofing

Heijerick et al. (2002) calculated that between 96 and 99.9% of the zinc from zinc roof runoff was in the dissolved phase. Athanasiadis et al. (2004) reported that 97% of the zinc in zinc roof runoff was in the dissolved phase. Golding (2006) reported between 70 and 100% of the zinc in the runoff from metal and PVC roofs 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 are. However, dissolved metals may be quickly bound by organic matter, reducing their mobility.

Other Roofing Materials

Concrete and Ceramic Tile Roofs

Concrete and ceramic tile roofs also contribute total metals, albeit at concentrations lower than those from galvanized or copper roofs (Table 1).

Persson and Kucera (2001) reported measurable concentrations of chromium, nickel, lead, and zinc in runoff from concrete tiles (Table 1). 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. Using 24-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 oxylates leached from the mixtures.

In Gdansk, Poland, Tobiszewski et al. (2010) reported PCBs in ceramic tile roof runoff at concentrations ranging from 1,327 to 303 ug/L of PCB, 52 in the first flush, and from 131 to 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

Asphalt shingle roofs have been reported to contribute lower zinc concentrations to runoff than zinc roofs (Table 1), but may have other contaminants that leach to stormwater. Clark (2010) and Mendez et al. (2010) reported measureable concentrations of arsenic from asphalt shingle roofs ranging from <0.01 to 1.4 ug/L. Mendez (2010) and Chang et al. (2004) measured both copper and lead in runoff from asphalt shingle 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.

Built-up, Flexible PVC, Rubber, Polyester, and Gravel Roofs

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 1). However, Good (1993) reported that a single sample taken from a built-up roof contributed 166 ug/L of copper; this was approximately 10 times the concentrations of copper 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 pollutants more readily than from asphalt applications. In a leaching test simulating rain, Clark et al. (2008a) reported that when exposed to a leaching test, roofing felt resulted in bis (2-ethylhexyl) phthalate (DEHP) at a concentration of 315 ug/L. DEHP, a plasticizing agent, is found not only in roofing felt (not generally exposed to precipitation after construction is complete), 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 Plexiglas. Pastuska (1985) reported that PVC plastic sheeting 0.8 mm thick (commonly used as an exposed roofing material in Poland) lost 8% of its plasticizers over 18 years, while the same material covered with gravel lost 16% over 9 years. Pastuska (1985) thought this differential was a result of gravel holding more moisture, mud, and bacteria which affect the loss of plasticizer. 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.

Vegetated Roofs

Vegetated roofs, and the materials used to construct 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 water that leaches through and runs off. Herrera (2011) reported median concentrations of copper and zinc from a vegetated roof in Washington at 7.5 and 20.3 ug/L, respectively. The Herrera study noted that vegetated roofs reduced both the concentrations and loadings compared with the painted Zincalume® roof that they evaluated.

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.

Preservatives in Roofing Materials

Treated wood shingles leach arsenic copper, lead, and zinc at potentially higher concentrations than untreated wood shingle roofs. 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 1,900 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, but ranging as high as 8,400 ug/L, in leachate from decking materials. CCA-treated wood shingles could also be expected to release arsenic, copper, and chromium to runoff, 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 manufacturers of the granules designed them to release copper over the life of the roof. Granules have been calculated to release between 560 and 640 ug/L of copper oxide (Everman and Joedicke, 2006).

Roofing materials may be treated with numerous other biocides to extend the useful life of the materials. Bucheli et al. (1998) found the herbicide 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, carbendazion, mecoprop, and Ingarol 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 peak concentrations ranging 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.

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. While, their research confirmed the leaching of constituents as a function of material composition, some of these materials (such as roofing felt) may not be exposed directly to precipitation.

Roofing Adhesives

Although not a part of this 2013 pilot study, adhesives can play an important role in roofing systems, especially in commercial roofing. Adhesives are used in both the installation and maintenance of roofs. Adhesives can serve as either the primary method of fastening roofing materials or may be used in combination with mechanical fasteners.

A wide range of adhesives are used by the roofing industry on the decking, insulation, and roofing material. They are often used to bond adjacent sheets, where roofing materials meet a vertical edge such as along HVAC systems, walls, skylights, and other areas. Single-ply roofing membranes require adhesives along the transition areas described above, even if mechanical fasteners are used as the primary attachment mechanism for the installation. Built-up roofing systems use the hot asphalt, torch down, or mastic along the transition areas.

Adhesives include solvent-based asphalt, solvent-based non-asphalt adhesives, water-borne asphalt emulsion adhesives, water-borne non-asphalt adhesives, polyurethane-based adhesives, and hot asphalt (SPRI, 1999). A review of material safety data sheets (MSDSs) for various adhesives provides examples of chemical ingredients commonly used:

- acetone
- toluene
- xylene
- ethyl benzene
- tert-butyl acetate
- hexane, methanol
- p-chloro-a,a,a-trifluorotoluene
- solvent naphtha (petroleum)
- acetic acid ethynyl ester
- cyclohexane
- n-heptane
- stoddard solvent
- 1,2,4-trimethylbenzene
- perchloroethylene
- methylene chloride
- tetrahydrofuran
- aromatic petroleum distillates

Although adhesives are used throughout roofing systems, they may not be exposed directly to precipitation. The main areas of likely exposure are along the seams, between sheets of roofing membranes, around drains and flashings, and at the edges of patches and corners. Most of the environmental exposure to the adhesives occurs during the installation of the roof as the solvents off gas as they dry. Exposure of wet product to precipitation is also reduced because roofing installations generally occur during dry summer months to minimizing the chance of water damage on unroofed structures.

Repairs often occur during the wet season because it is often during rains when the leaks become apparent. Thus, patching and other roof repair can expose adhesives to precipitation and their constituent chemicals may leach into runoff. The leaching of constituents in the adhesives varies based on the product composition and application practices. MSDSs and specifications can direct roofing repair teams to practices that can lead to environmental contamination. For instance, in their specification sheet, the Henry Company (2009) describes product leaching that occurs and recommends washing excess product into the environment.

> “This adhesive, like all asphalt-based products, forms a small amount of water soluble material as it weathers. Normally this is not noticeable because the rain washes it away. However, roofs having a pitch less than ½” per foot, or ones having poor drainage, will accentuate the problem by concentrating the water soluble material in low spots. If there is no rainfall, hose roofs off to remove the water soluble material. Frequent inspection of these roofs is recommended because abnormally rapid deterioration of any roofing material may occur where water stands for a long period of time.” (Henry Company, 2009)

Ultimately, the chemical constituents of adhesives and application practices should be evaluated to reduce environmental impacts.

Other Factors Affecting Contaminants in Roof Runoff

pH

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. The pH of the rain plays a more prominent role in metal roofs or roofs containing metals in their matrix. 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 from copper and zinc roofs during both first-flush and steady-state runoff with decreasing pH. They attributed this result to the greater solubility of copper and zinc corrosion products at lower pH. Bielmyer et al. (2011) also evaluated the impacts of pH using simulated rain water. At a pH between 4.5 and 5.8, the median total copper concentrations measured were 433 and 76 ug/L for copper panels (troughs) 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 10 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 rain water 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. They also reported that runoff rates are a function of the corrosion rate; thus, they measured significantly higher runoff loads in the highly industrialized areas of Belgium, than in Stockholm, Sweden. They noted that since sulfur dioxide concentrations had been reduced under more recent environmental regulations, leading to generally lower corrosion rates and runoff loads than 50 years ago.

Rainfall Intensity

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). The 8 mm/hr and 20 mm/hour intensities showed no differences. This is in line with the work by Odnevall Wallinder and Leygraf (2001) who reported that copper dissolution rates were a function of relative humidity, and drizzle is often associated with highly humid air. Additionally, these authors demonstrated that copper and zinc runoff loading in terms of ug/m^2 of roof was a function of precipitation depth.

Jungnickel 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

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 (under windless conditions), steeper roofs allow more rapid flow from the exposed surface area and reduced contact time with the rain. Thus the 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. Bielmyer et al. (2011) observed that concentration of copper was a function of the median run length of the synthetic rain drops, and was thus related to the length of the copper trough (panel). The authors further concluded that run length was of greater importance than either slope or orientation. When comparing metals concentrations from roofs, the length of the roofs should be considered.

Orientation

Orientation of the roof to the prevailing wind and rain can influence the metals concentrations in runoff. Odnevall Wallinder et al. (2000) found that metals loadings in runoff from roofs were also a function of the direction of the prevailing wind, as a greater volume of rain actually hits the surfaces facing the prevailing direction.

Metals in Marine Environments

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 than found at the inland site which had less frequent wet and dry cycles for dissolution and re-precipitation. The authors have reported that the metals in roof runoff were predominantly in the dissolved phase, implicating dissolution as a major vehicle for liberating metals in runoff.

Aerial Deposition

Contaminants associated with wet and dry air deposition comprise a portion of roof runoff. For example, Sabin et al. (2004) found that more than 50% of the metals in stormwater runoff in Los Angeles was 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 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 that had exposed metals stored on site or within the product (e.g., wood preservers).

A recent study of the Puget Sound basin evaluated heavy metals, PAHs, and other compounds in wet and dry atmospheric deposition. This study found 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., 2012). The relative contribution of pollutants associated with wet and dry deposition has not been compared with concentrations in runoff from roofing materials within the Puget Sound basin.

To differentiate between material 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; their results may have been affected by dry deposition of metals from a local fertilizer manufacturer. Clark (2010) and Chang et al. (2004) subtracted both wet and dry aerial deposition.

Purpose of the Study

Based on generalized conclusions from the Puget Sound Toxics Assessment (Ecology, 2011a) and the literature review, Ecology needed to gain a better understanding of region-specific information related to contaminant levels in roof runoff from various roofing materials. The present 2013 study was designed to provide better information to assess contaminants from roofing materials in the Puget Sound basin by collecting data using:

- Region-specific roofing materials.
- Region-specific runoff based on actual climatic conditions in the Puget Sound area.
- Controls for factors such as concentrations of contaminants in atmospheric deposition.

This study focused on obtaining the 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 gutters and downspouts, HVAC systems, flashings, exposed fasteners, and post-manufactured treatments, to name a few. This pilot study offered the first step in a systematic approach to assessing toxics in roofing systems by assessing only specific types of roofing materials (those most commonly used in the region) and by controlling for as many variables as possible. This study also focused only on new roofing materials (i.e., un-aged materials) that were provided and installed by the manufacturers and their contractors at the beginning of the study.

Objectives

The primary objectives of this study were to determine:

- The range of concentrations of specific chemicals leached from selected new roofing materials used in the Puget Sound basin by analyzing runoff from these roofing materials.
- The range of loadings of specific chemicals leached from selected new roofing materials on the basis of unit surface areas and the depth of precipitation.

- Whether new 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 was to determine:

- Whether post-manufactured coatings can reduce leaching from specific roofing materials.

Roofing Task Force

The design of the study included input from a Roofing Task Force (RTF) of manufacturers, contractors, roofing associations, and other stakeholders. Ecology asked RTF participants to provide input on the design of the study, the chemicals of concern, and the types of roofing to be evaluated. The RTF also provided study direction and comments on the draft Quality Assurance (QA) Project Plan resulting in the final approved QA Project Plan (Ecology, 2013a). Industry representatives on the RTF selected the specific products tested and donated the roofing materials and installation. Thus, the roofing materials assessed do not necessarily represent a random selection of materials available in the Puget Sound basin.

How Study Results Will Be Used

This study represents Ecology's initial investigation specific to roofing materials and as such serves as a pilot study. Ecology is continuing to collect and analyze runoff from the roofing panels from 10 additional rain events in the fall of 2013 and winter of 2014.

Neither this study nor the supplemental information from the second round of sampling will recommend specific products for use by the roof manufacturing community, construction contractors, roofing designers, homeowners, or others. In addition, the results are not intended to help make decisions or recommend treatment practices for reducing 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 better understand the role of roofing systems in releasing toxic chemicals within the Puget Sound basin.

Methods

Summary of Study Design

The major portion of this 2013 pilot study evaluated stormwater runoff from 18 constructed, pilot-scale roof panels. Ecology constructed all of the roofing support frames to the same size (4 feet by 8 feet). Roofing manufacturers provided the actual roofing materials and specialists who installed the materials on the panels. Appendix A provides descriptions of the roofing materials and installation details. Ecology conducted X-ray fluorescence screening to ensure that the metals and bromine content of roofing materials installed were within the range of commercially available roofing materials.

Another aspect of this project evaluated the potential for post-manufacturer applied coatings to reduce the copper and zinc released to stormwater. Ecology prepared “coupons” (small samples) of copper, galvanized steel, and Zincalume® with and without coatings and exposed these to the synthetic precipitation leaching procedure (SPLP). The leachate was assessed for metals and organics (PAHs, phthalates, and PBDEs).

This section describes the following project elements:

- X-ray fluorescence (XRF) analyses of samples and roofing materials.
- The pilot-scale roofing materials assessment and procedures that differed from those described in the QA Project Plan for the pilot-scale roofing panel portion of the study.
- Preparation of samples for the SPLP used to assess the relative effectiveness of post-manufactured coatings at reducing leaching from metal roofs.
- A single leaching test used to assess leaching of phthalates from HDPE samples.

XRF Analysis

Roofing manufacturers and associations met to determine the products they believed best represented the roofing materials market in the Pacific Northwest that they were willing to donate and install for the pilot-study roofing assessment. To ensure that the specific manufacturer-selected roofing materials installed were within the range of products available for a roofing type, Ecology conducted XRF analyses on a variety of products donated by the manufacturers in coupon-sized samples as well as on the installed pilot-study roofing materials.

Manufacturers submitted samples of various types of roofing. Each sample arrived usually in a plastic bag, and labels were within the bags or otherwise associated with a specific sample. Ecology maintained the samples in their labeled containers until each was removed for XRF analysis.

The Thermo Fisher Scientific Niton XRF Analyzer, used for the XRF analyses, emits x-ray radiation to determine the metal and bromine composition of each sample. (Bromine is an indicator of the presence of brominated flame retardants.) The penetration of the x-rays depends on the density of the material and ranges from 0.05 to 2 millimeters. While this depth of penetration assesses an integrated composite of the materials, including those portions not necessarily exposed to potential precipitation, it is useful for comparing the coupons with the materials installed on the panels. The XRF results of the coupon analyses were compared to a field XRF analysis of the installed panels to determine whether metals and bromine concentrations of the installed panels were within the ranges of the coupons.

Pilot-Scale Roofing Assessment

The study evaluated runoff from 18 constructed pilot-scale roof panels including two glass control panels. Table 2 lists the roofing material types by slope and the measured surface areas exposed to precipitation of each roof. All roofing panels faced south-southwest, the direction of the prevailing wind. Steep-slope roof panels were installed at 26.5^{o} 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). The low-slope roofs were installed at 1.2^{o} (known as ¼:12 in the industry), typical of commercial roofs. The identification codes listed in Table 2 are used in subsequent tables and figures of this report to refer to roofing materials installed on the panels. Appendix A provides descriptions of each of the panel types and their installation, and Figure 1 depicts the layout of the site.

Ecology constructed all roofing assemblages to the same size (4 feet by 8 feet). With the assistance of the Roofing Task Force, Ecology selected a total of 14 types of roofing materials for the pilot study. The manufacturers selected the specific products donated and installed for the study. Thus, the roofing materials assessed do not necessarily represent a random selection of available materials.

Roofing specialists installed the roofing panels between January 22 and 28, 2013, at the Ecology headquarters facility in Lacey, Washington. Ecology installed two glass control panels, one at steep slope and one at low slope.

To assess variability, three replicates of the asphalt shingle without algal-resistant (AR) copper-containing granules were constructed. This roofing material was selected for replication as it represents 71% of the roofing used in the Puget Sound basin (Ecology, 2011a). Asphalt shingles without AR represent the largest proportion of market in the Pacific Northwest, primarily because the AR does not deter moss growth which is a greater problem than algae growth in the region (Dinwiddie, pers. comm., 2013).

Each of the asphalt shingle panels without AR was installed using shingles donated from the six asphalt shingle manufacturers in the Pacific Northwest. Thus the shingles installed on the three replicate panels represented a wide array of variables such as asphalt source, mineral composition, and manufacturing process differences. The rows of shingles were arranged in a random order on each of the three panels. Similarly, the shingles used for the asphalt shingle panel with AR also represented the six asphalt shingle manufacturers in the Pacific Northwest.

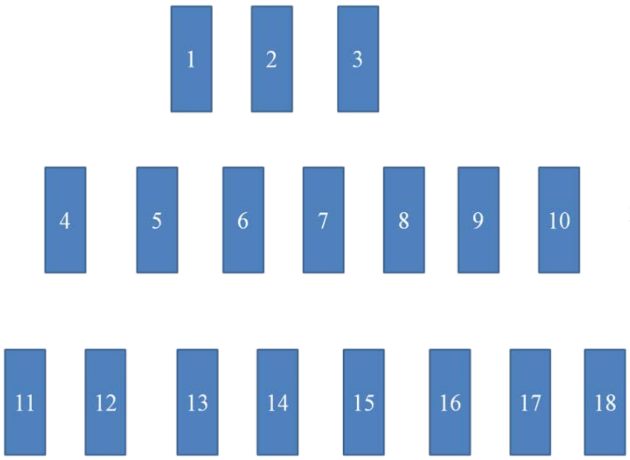
Table 2. Roofing materials, identification codes, and panel surface areas.

ID Code	Roof Material	Surface Area Exposed to Collected Precipitation	
		Feet^2	Meters^2
Steep-Slope Panels			
AAR	Asphalt shingle - composite of 6 types of shingles with algae resistant (AR) copper-containing granules	33.2	3.09
AS-1 AS-2 AS-3	Asphalt shingle - composite of 6 types of shingles without AR copper-containing granules*	33.5 33.3 33.3	3.12 3.09 3.09
CPR	Copper	32.8	3.05
CTI	Concrete tile	32.1	2.98
PAZ	Manufacturer-painted galvanized steel, painted with silicone-modified polyester paint	33.1	3.08
TWO	Manufacturer-treated wood shake	33.6	3.13
WOS	Wood shingle	33.6	3.13
GST	Frosted glass (control) at steep slope	32.0	2.98
Low-Slope Panels			
BUA	Modified built-up roof with Atactic polypropylene (APP) granulated cap sheet	33.8	3.14
BUR	Built-up roof with oxidized asphalt granulated cap sheet	33.4	3.11
BUS	Modified built-up roof with styrene butadiene styrene (SBS) granulated cap sheet	33.5	3.12
EPD	Ethylene propylene diene monomer (EPDM)	32.7	3.04
PVC	Polyvinyl chloride (PVC)	32.8	3.06
TPO	Thermoplastic polyolefin (TPO)	32.5	3.02
ZIN	Zincalume® (a trade name for Galvalume)	33.0	3.07
GLO	Frosted glass (control) at low slope	32.1	2.98

* Results of these replicates were systematically averaged in this study and denoted as AS^A.

All panels were exposed to the same precipitation events and the same wind direction simultaneously. Ecology collected and analyzed runoff from roof panels from 10 rain events between February 22 and April 19, 2013, in accordance with the QA Project Plan (Ecology, 2013a). Appendix B describes minor variations in procedures from the QA Project Plan. Ecology's Manchester Environmental Laboratory (MEL) analyzed samples for metals (arsenic, cadmium, copper, lead, and zinc), PAHs, phthalates, and PBDEs.

Roof Type Location



1-3	Asphalt shingle
4	Painted galvanized metal
5	Treated wood shake
6	Asphalt shingle with AR
7	Copper
8	Untreated wood shingle
9	Glass steep-slope (control)
10	Concrete tile
11	Zincalume ®
12	PVC
13	Modified BUR with SBS cap sheet
14	EPDM
15	BUR with oxidized asphalt cap sheet
16	Thermoplastic polyolefin
17	Modified BUR with APP cap sheet
18	Glass low-slope (control)

Figure 1. Aerial photograph of study site layout.

Rain gage is located between steep-slope and low-slope roofs on right side of photograph.
Department of Ecology Headquarters building is in the background.
Photograph provided courtesy of Russ McMillan, Department of Ecology.

Decontamination

Ecology staff decontaminated the panels, gutters, and sample collection equipment as described the QA Project Plan with the minor differences detailed in Appendix B. Minor differences did not affect the outcome of the study.

Sample Collection

Staff targeted rain events for sampling when the weather forecast predicted at least 0.1 inch of precipitation in a 24-hour period. Weather reports were reviewed daily to determine whether six hours had elapsed since the preceding event with less than 0.1 inch of precipitation and whether the rain event was predicted to be of sufficient size (a qualifying rain event, i.e., greater than 0.1 inch). When these criteria were met, and based on the best professional judgment of the staff concerning weather predictions, the 304-grade stainless-steel sample collection containers were deployed.

If sample volume approached the maximum collection-container volume (56.8 liters), staff recorded the time and quickly removed the gutters from the apparatus, ceasing runoff collection. Sample collection containers were not allowed to overflow. For some events, sampling was stopped to maintain the defined 24-hour limit of a rain event or to control the volume of the event. Ice baths surrounded the stainless-steel sampling containers to maintain near ambient temperatures.

For each rain event, the runoff in the stainless-steel container was mixed prior to and during sampling. Where split samples and matrix spike/matrix spike duplicate samples were obtained, they were pumped from the stainless-steel container using the same mixing procedure as the original sample. Replicate samples were obtained from the three asphalt shingle panels; these were sampled individually. Appendix B provides details of sampling procedures including where they differ from the QA Project Plan (Ecology, 2013a). Runoff in each of the stainless-steel containers was measured for depth, and tested for pH, temperature, and specific conductance using calibrated meters. Appendix C provides the field notes with the rain gage records, as well as pH, temperature, and conductance values.

Sample Processing

Samples were preserved, labeled, stored in coolers on ice, and placed in a walk-in refrigerator awaiting transport to MEL. Staff followed the chain-of-custody procedures, alerted MEL staff of the need for sample delivery, and ensured that field notes were completed. MEL reported the data, which were complied into data tables (Appendix D). MEL provided results in pdf format (Appendix E) and in electronic format (Appendix F).

Synthetic Precipitation Leaching Procedure (SPLP)

To determine the effectiveness of the coatings at reducing metals leaching, Ecology assessed coupons with and without post-manufacturer applied coatings. To determine whether coatings could leach organic contaminants, thereby exchanging release of one toxic compound for another toxic compound, not achieving a net environmental benefit, Ecology also analyzed PAHs, phthalates, and PBDEs in the leachate.

Because no galvanized steel roofing panel was assessed as part of the pilot study, Ecology also compared the leaching from a galvanized steel coupon to that of a Zincalume® coupon. This assessment was also conducted to determine the utility of the method for future studies. The testing of coupons, rather than large panels, was used in this portion of the study to manage costs. Table 3 lists the coupon materials, surface areas, coatings, and weights of the applied coatings.

The U.S. Environmental Protection Agency (EPA) designed the SPLP method (EPA method 1312) to assess the potential for contaminants to leach in a simulated rain medium during an 18-hour to 20-hour period of tumbling. The resulting leachate is then analyzed. The EPA procedure was modified for this study as described in the QA Project Plan (Ecology, 2013a).

In this study, the leachate was analyzed for five total metals (arsenic, cadmium, copper, lead, and zinc), PAHs, and phthalates. For the galvanized steel coated with Elastuff™ 101, three additional coupons (samples EPB-04 through EPB-06) were exposed to the modified SPLP procedure and analyzed for PBDEs, as PBDEs were suspected constituents used in formulating this coating. Details of the SPLP analysis are described in Appendix B.

HDPE Leaching Analysis

No literature assessment could be found of whether or not high density polyethylene (HDPE) materials leach phthalates on exposure to water. While the gutters used in this study for collection of runoff were constructed of HDPE lined with Teflon®, staff were concerned that the thin Teflon liner could eventually become damaged, exposing the runoff to the HDPE. Thus staff conducted a single test by exposing four samples of HDPE with a total surface area of 13,322 mm^2 into 1.7 liters of distilled, deionized (DI) water from MEL for 24 hours. A sample of the water was analyzed for phthalates.

Table 3. Coupon materials, coating types, and identification codes.

Materials and Sealants	ID Codes
Zincalume®, uncoated	ZIN-01
	ZIN-02
	ZIN-03
Galvanized steel, uncoated (Galvanized steel was not assessed in the panel pilot study)	GAL-01
	GAL-02
	GAL-03
Galvanized steel coated with Ames Research Laboratory Inc. Snow Seal™	SNO-01
	SNO-02
	SNO-03
Galvanized steel coated with Sherwin Williams SHER-CRYL™ HPA High Performance Acrylic Semi-Gloss Coating	ASW-01
	ASW-02
	ASW-03
Galvanized steel coated with Sherwin Williams UNIFLEX® Elastomeric Roof Coating	ESW-01
	ESW-02
	ESW-03
Galvanized steel coated with Coatings & Foam Solutions Poly-Sil 2500 High Solids	SIL-01
	SIL-02
	SIL-03
Galvanized steel coated with Karnak® Fibered Aluminum Asphalt Coating 98AF	ALA-01
	ALA-02
	ALA-03
Galvanized steel coated with Quest Construction Products Elastuff™ 101	EPB-01
	EPB-02
	EPB-03
	EPB-04
	EPB-05
	EPB-06
Copper, uncoated	CUB-01
	CUB-02
	CUB-03
Copper coated with Syncrylac®	SYN-01
	SYN-02
	SYN-03
Copper coated with PPG Architectural Finishes Coraflon® ADS Intermix	COR-01
	COR-02
	COR-03

Laboratory Analysis and Data Quality

The QA Project Plan (Ecology, 2013a) outlines the quality control and quality assurance process for this roofing study. The following is a summary of the quality control measures.

Quality control (QC) is often confused with the term *quality assurance* (QA). QC refers to a set of standard operating procedures for the field and laboratory that are used to evaluate and control the accuracy of measurement data. QA is a decision-making process, based on all available information, that determines whether the data are usable for all intended purposes (Lombard and Kirchmer, 2004).

The data quality objectives and measurement quality objectives described in the QA Project Plan were generally met. The subsequent subsections give an overview of the procedures, describe any substantive differences from the QA Project Plan, and describe whether these differences had an impact on the quality of the data.

Field QC Samples

For the first three rain events, Manchester Environmental Laboratory (MEL) analyzed runoff samples from all panels for total and dissolved metals (arsenic, cadmium, copper, lead, and zinc), PAHs, phthalates, and PBDEs. Thereafter, panels were analyzed for a more limited suite of analytes in accordance with the QA Project Plan (Ecology, 2013a). Table 4 lists the analytical methods used. Table 5 lists the analyses by panel type for the remaining seven rain events.

Table 4. Analytical methods used.

Parameter	Analytical Method
Total metals	EPA Method 200.8
Dissolved metals	EPA Method 200.8
PAHs and phthalates	SW-846 Method 8270 Selective Ion Method (SIM)
PBDEs	SW-846 Method 8270D

Table 5. List of analyses conducted by roof type for final seven rain events.

Analytes	Steep-Slope Panels								Low-Slope Panels							
	AAR	AS1-AS3	CPR	CTI	PAZ	TWO	WOS	GST	BUA	BUR	BUS	EPD	PVC	TPO	ZIN	GLO
Total Metals	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
PAHs & Phthalates	✓	✓						✓	✓	✓	✓	✓	✓	✓		✓
PBDEs								✓				✓	✓	✓		✓

Shading indicates glass control panels.
Panel identification codes are defined in Table 2 on page 40.

QC samples were obtained for each rain event. For every storm, all three of the asphalt shingle panels were sampled as replicates. Replicates allow assessment of the variability (precision) associated with the three roofing surfaces.

For the other panels, staff obtained field split samples; these served as laboratory replicates. Field splits serve to assess variability of the matrix (stormwater) and the ability of the mixing regime to ensure homogeneity of the samples. Field splits also allow assessment of the variability in the laboratory analysis.

Matrix spike samples and matrix spike duplicates were obtained at the same locations as the field splits depicted in Table 6. Equipment rinse blanks were obtained for each sampled event as described in Appendix B.

Table 6. Schedule of field split and matrix spike/matrix spike duplicate samples taken by rain event.

Event #	Date (2013)	All Parameters	Metals	PAHs/ Phthalates	PBDEs
1	Feb 22	CPR, AS1, BUA*			
2	Feb 25	PAZ, GST, EPD			
3	Feb 28	TWO, AAR, TPO			
4	Mar 6	EPD, GST, GLO			
5	Mar 12	GST, TPO, PVC			
6	Mar 13	EPD, GLO, DIW			
7	Mar 20		AS-2, BUR, WOS	AS-2, BUR	PVC
8	Apr 5		AS-3, BUS, ERW	AS-3, BUS, ERW	ERW
9	Apr 11		CTI, AAR, CPR	AAR, AS-2, BUA	GLO
10	Apr 19		PAZ, TWO, PVC	BUR, PVC, TPO	PVC

DIW: Distilled, deionized water blank
ERW: Equipment rinse blank
* Error in labeling; no MS/MSD was conducted on this sample only 3 field splits.
Panel identification codes are defined in Table 2 on page 40.

Laboratory QC

MEL conducted the laboratory analysis and laboratory QC. MEL also provided data QA in the form of narrative reports. Appendix E provides the narrative reports. Generally, MEL met the data quality objectives (DQOs) and measurement quality objectives (MQOs) described in the QA Project Plan (Ecology, 2013a), with the minor exceptions described in Appendix B. These exceptions did not result in a completeness of less than the 90% prescribed in the QA Project Plan. While the laboratory data were qualified as described in the subsequent paragraphs, they were deemed useable to meet the objectives of this study.

Data Qualifiers

Ecology’s technical lead conducted overall project QA. As qualified, all laboratory data were determined useable for the purposes of this study. To provide the reader with rationale for data qualifiers, the reasons for qualified and flagged results are described at the beginning of Appendix F. Each of the flags applied in the final two columns of the Excel spreadsheets in Appendix F could be used individually or in combination with one another to depict the reason(s) for a qualified result. These more detailed qualifiers are provided to give the reader a better understanding of the data and are listed only in the electronic data deliverables (Appendix F).

Generally, data flags other than J [analyte detected between the method detection limit (MDL) and the reporting limit (RL)] or U (analyte not detected at the MDL) ranged from 3% to 13% of the results, except for flags due to method blank contamination. Method blank contamination, particularly for phthalates, resulted in 20% to 31% of the results receiving a qualifier and elevated detection limits. Laboratory contamination is discussed further in the subsequent section.

For the data tables in the body of this report and in Appendix D, the more standard J, U, and Rej flags are used to represent analytes whose values are estimated for any reason, analytes that were not detected at the MDL, and analytes who results were rejected, respectively.

Laboratory and Field Contaminants

Organics Analysis

PAHs and phthalates were detected in many of the method blanks and occasionally in the equipment rinse blanks. Phthalates, and to a lesser extent PAHs, are ubiquitous laboratory contaminants, particularly when methods are designed to detect concentrations in the parts per trillion range. At these very low detection limits, laboratory contaminants can mask the results of the samples. The reduced frequency of detection of phthalates above the concentrations that were five or more times the method blanks in storms 5 through 10 may be an artifact of the fact that phthalate concentrations in the method blanks gradually increased over the duration of the project. Organics results with concentrations less than or equal to five times the method blank (laboratory contaminant threshold), or the equipment rinse blanks, were qualified as undetected.

PAHs and phthalates were analyzed using EPA method 8270SIM. This method allows compounds to be detected at concentrations between 10 and approximately 90 parts per trillion. Many of the analytes are ubiquitous in the environment at low levels. Differentiating between both background contamination (“noise”), the capability of the instrumentation, and actual analytes released from roofing materials is difficult at these low concentrations. Future analyses with a less sensitive method such as 8270D would serve as a more cost-effective screening tool to identify differences among roofing materials (e.g., as they weather).

Metals Analyses

Concentrations of metals were occasionally detected in the equipment rinse blanks, distilled deionized (DI) water blanks, and the laboratory method blanks. Potential sources of the equipment rinse blank contamination include the DI water used for decontamination, metals associated with the stainless-steel sampling containers, the mixing device, or measuring device.

Ecology analyzed the concentrations of metals in the DI water blanks. The laboratory provided the DI water, which was used for both the decontamination procedure described in the QA Project Plan (Ecology, 2013a) and as water to obtain the equipment rinses.

DI water blanks included trace concentrations of total metals between 10 and 100% of the sampling events. Copper and zinc were detected in the DI water blanks in 100% of the events. Concentrations in the DI water blanks represented between 11 and over 100% of the concentrations measured in the equipment rinse blanks. For example, on an event-by-event basis, zinc concentrations in the DI water blanks represented between 12% and more than 100% of the zinc in the equipment rinse blanks. Given the DI water contributed a portion of contaminants measured in the equipment rinse, detections in the equipment rinse blanks were not thought to reflect only contaminants contributed by the equipment. The metals results were therefore qualified differently. Metals in the runoff samples with concentrations less than or equal to five times the equipment rinse blank, or those elevated method blanks were qualified as estimated (J-flagged), rather than non-detected.

Variability

Variability in concentrations in the runoff among storms is typical for stormwater data. Stormwater runoff concentrations typically exhibit a greater range of concentrations than ambient surface waters. Variability is due to numerous factors such as rainfall amount and intensity, season, amount of aerial deposition that accumulates between storms, land uses, sampling bias towards first-flush or not, to name a few.

Ecology reduced sampling variability by collecting 100% of the runoff. Sub-sampling variability was minimized by mixing before pumping aliquots into sample containers and assessed using field splits. Despite the design scheme to reduce variability, Ecology observed wide variability of concentrations in the runoff samples between split samples.

Ecology calculated the relative standard deviation (RSD) for split samples and for replicates from the three asphalt shingle panels, rather than the relative percent differences (RPDs) as described in the QA Project Plan (Ecology, 2013a). RSDs are routinely calculated for three or more replicates. For comparability and consistency, RSDs were calculated for both field splits and for the three field replicates. Ranges, median, and mean values of the RSDs are presented by analyte in Appendix G.

Where average RSD for a parameter exceeded the QA Project Plan prescribed goals (20% for metals and 40% for organics), substantially lower medians indicated the presence of a few outlier RSDs. The maximum variabilities between split samples (maximum RSD values) were generally observed at the lowest concentrations. Where reported values are generally less than five times the reporting limit (RL), Mathieu (2006) has determined that RSDs are higher than generally established for ambient monitoring. This is particularly the case for the organics data, where the greatest variability appears (Table G-1 in Appendix G).

The variability in the split samples indicate that the mixing technique may not have created the level of homogeneity anticipated, especially when concentrations were between the MDL and RL. The variability in the split samples could also be attributed to a reduced precision of the analytical technique at concentrations between the MDL and RL. Variability would be reduced by assessing only values greater than the RL; however, information may be lost in this fashion.

Ecology also calculated RSDs for the replicates from the three asphalt shingle panels to ensure that the random placement of the six types of shingles did not affect the results (Table G-2 in Appendix G). Again, where average RSD for a parameter exceeded the QA Project Plan prescribed goals, substantially lower medians indicated the presence of a few outlier RSDs. For the field replicates, the RSDs were lower for the organic compounds. No data were rejected based on the RSDs.

Assessing the RSDs of the replicates identifies not only variations among the three asphalt shingle panels but also variations in mixing, sampling protocols, and analytical techniques. Ecology's sampling protocols minimized these potentially confounding factors.

A subsequent evaluation of the metals from each of the three asphalt shingle panels revealed that AS-3 had significantly higher concentrations of total copper than AS-2. Other comparisons revealed no statistically significant differences. The outcome of this subsequent investigation is described in the *Discussion* section.

Summing Organic Constituents

PAHs, phthalates, and PBDE congeners were generally very low in concentration and spatially heterogeneous. To determine possible patterns that included all the compounds within a category, Ecology calculated the detected sums of each category of organic compound (i.e., PAHs, phthalates, and PBDEs) for each panel type and each rain event. Staff calculated the sums by adding concentrations that were either qualified[1] (J flagged) as estimates and those that were reported above the RL. This methodology follows the guidance provided by Era-Miller and Seiders (2008).

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[1] Data are qualified or J flagged for a variety of reasons including: results with concentrations between the MDL and RL; contamination in the method blank or equipment rinse blank; exceedance of method-prescribed holing times; failure to meet QA objectives in the QA Project Plan.

Where the laboratory reported a detected compound in one sample but not in the replicate or split sample, staff calculated the average by using one-half of the concentration of the MDL for the undetected value. This approach differs from a common approach to use either the RL or the MDL for the undetected value. Either of those two values would lead to an overestimate of the total PAHs. Since the compound was detected in one sample at least at the MDL, it is likely to have been present but at a value less than the MDL. Use of one-half of the MDL may artificially inflate the total calculation but less than use of either of the other two values. Use of either the RL or the MDL for these calculations would not improve the ability to differentiate among runoff concentrations from the different panels.

Results

X-Ray Fluorescence

Table 7 gives the ranges of the XRF results of the manufacturer-provided samples ("coupons") of roofing materials. The XRF measured a long list of metals and bromine. The pertinent analytes for this study included arsenic, cadmium, chromium, copper, lead, zinc, and bromine. Ranges of each of these analytes are presented in Table 7 for the coupons and Table 8 for the roofing materials installed on the pilot-study panels.

The XRF results were intended to serve as an indicator of whether the roofing materials installed for the pilot study were similar in chemical content to materials typical of the industry. The XRF analyses served as a screening test, limited by the accuracy of the instrument. The XRF values are provided from the instrument in parts per million. Standard errors ranged from less than 1% of the results, where results were extremely high (for example, for copper in the copper materials), to more than 100% of the values where concentrations were low concentrations. Thus identified differences between the coupons and materials installed on the panels were only identified when ranges differed by more than 100%.

With few exceptions, the installed panel materials were within the range of the metals concentrations in the coupons, considering the sensitivity of the XRF unit. Exceptions included:

- One of the asphalt shingle coupons without algae resistance (AR) contained extremely high copper concentrations (more than 19,000 parts per million or ppm of copper). This coupon was re-measured with results at more than 17,000 ppm copper. Ecology attempted to identify the source of this discrepancy and concluded that this coupon appeared to be an outlier as the next highest asphalt shingle coupon was 562 ppm. The outlier value was not included in Table 7.
- The asphalt shingle coupons with AR contained higher concentrations of zinc and lower concentrations of chromium than the installed panel materials.
- The asphalt shingles coupons with and without AR contained higher zinc concentrations than the installed panel. These may be due to differences in the native material and processing.
- The installed painted galvanized metal panel (PAZ) contained substantially higher concentrations of chromium and bromine than the polyester, silicone-modified polyester, or acrylic painted galvanized coupons. These differences may be a function of either differences in the specific paint that was applied to the coupons compared to the panel, or differences in the thickness of the underlying chromated layer.
- The BUR with SBS cap sheet coupons had zinc concentrations as high as 2,548 ppm, which was higher than the installed panel. This difference may be a function of the variability in either asphalt or the granular cap materials.
- The installed EPDM panel was generally lower in zinc concentrations than the range in the coupons, particularly than the upper end of the range of the coupons.

- In the PVC coupons, zinc concentrations were below detection, while the roofing material installed on the panel ranged from 208 to 270 ppm zinc. Zinc may have been added to the formulation on the installed panel as a biocide.
- In TPO coupons, bromine was detected as high as 535 ppm, while none was detected in the installed TPO panel material. Hubbard (pers. comm., 2013) indicated that some of the coupons included flame retardant while the roofing material installed on the panel did not.

The XRF analyses of the coupons and the installed roofing materials demonstrated that there was variability between products within a specific roofing type, within the limitations of the XRF screening tool. However, the roofing materials installed on the panels were generally characterized by the coupons. The differences between coupons and installed panels can generally be attributed to manufacturing differences. The XRF screening served its intended purpose.

Subsequent XRF Analyses of Asphalt Shingle Panels

After the analytical results of the runoff were obtained, Ecology re-assessed the concentrations of copper on the three asphalt shingle panels, at the suggestion of the Roofing Task Force. For each panel (AS-1 through AS-3), three XRF readings were obtained from each of the six shingle types (provided by six different manufactures) that had been randomly installed on the panels. Only one type of shingle had concentrations of copper above 70 ppm, and those ranged from 166 to 629 ppm. The higher (and more variable) concentrations in the one shingle type may be a function of differences in manufacturing processes.

The three XRF readings from each panel for each shingle type and each metal were averaged. The highest average copper concentration was found on panel AS-3 (464 ppm compared to 396 ppm on panel AS-1 and 371 ppm on AS-2). This difference will be further assessed in the *Discussion* section.

Table 7. Ranges of concentrations (in ppm) of metals and bromine from XRF analysis of roofing material coupons.

Roof Type	No. of Samples	Arsenic	Cadmium	Copper	Chromium	Lead	Zinc	Bromine
Steep-Slope Coupon Types								
(AAR) Asphalt shingles with AR	11	< LOD-12	< LOD	< LOD-14,820	< LOD-788	< LOD	6 - 1,130	< LOD-10
(AS) Asphalt shingles without AR	6	< LOD -14	< LOD-16	< LOD-562	< LOD-1,901	< LOD-25	5 - 1,279	< LOD
(CPR) Copper	2	NM	< LOD	998,854-998,295	< LOD	< LOD	< LOD-578	< LOD
(CTI) Concrete Tile	6	NM	< LOD	< LOD	< LOD	< LOD-14	44 -60	< LOD
Polyester painted galvanized metal	3	NM	< LOD	6,019 – 6,322	34,046-34,575	< LOD	675,110-723,460	< LOD
(PAZ) Silicone-modified polyester painted galvanized metal	3	NM	< LOD	669 - 33	9,429-9,755	< LOD	685,962-723,825	< LOD
Acrylic painted Galvalume®	2	NM	< LOD	293 -4 02	831-995	< LOD	533,160-723,825	< LOD
(TWO) Treated wood shake	2	1,003-1,524	< LOD	645 - 933	3,552 - 4,432	< LOD	< LOD	< LOD
(WOS) Wood shingle untreated	3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Wood shake with fire retardant	2	< LOD-11	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Low-Slope Coupon Types								
(BUA) BUR with APP cap sheet	32	< LOD	< LOD-18	< LOD-59	< LOD-211	< LOD-75	< LOD-26	< LOD-6
(BUR) BUR with oxidized asphalt cap sheet	1	NM	20	< LOD	80	22	107	< LOD
(BUS) BUR with SBS cap sheet	28	< LOD	< LOD-20	< LOD	< LOD-268	< LOD-28	30 -2,548	< LOD- 6
(EPD) EPDM	13	ND-19	< LOD-15	< LOD-48	< LOD-256	< LOD-41	6,512 - 26,835	< LOD-36
(TPO) Thermoplastic polyolefin	15	< LOD-43	< LOD-16	< LOD	< LOD-76	< LOD-54	< LOD-54	< LOD-535
(PVC) Polyvinyl chloride	30	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Galvanized metal	9	NM	< LOD	< LOD-352	265 - 1,784	< LOD	654,314 - 914,236	< LOD
(ZIN) Galvalume® & Zincalume®	12	NM	< LOD	< LOD-473	539 - 1,355	< LOD	485,933 - 568,693	< LOD

LOD: Limit of detection
NM: Not monitored by XRF unit due to unit error

Table 8. Ranges of concentrations (in ppm) of metals and bromine from XRF analysis of roof panels.

Roof Type	No. of Samples	Arsenic	Cadmium	Copper	Chromium	Lead	Zinc	Bromine
Steep-Slope Panels								
AAR (Asphalt shingles with AR)	6	< LOD-32	< LOD	82-10,215	< LOD-1,277	< LOD	< LOD-522	< LOD
AS (Asphalt shingles without AR)	6	< LOD-13	< LOD	< LOD-103	< LOD-733	< LOD–15	< LOD-68	< LOD
CPR (Copper)	2	< LOD	< LOD	995,552-999,397	< LOD	< LOD	< LOD-3,173	< LOD
CTI (Concrete tile)	3	< LOD-17	< LOD	< LOD	< LOD	< LOD	< LOD-49	< LOD
PAZ (Painted galvanized metal)	2	1,400	< LOD	< LOD	88,910-91,712	< LOD	760,689-772,256	83-1,347
TWO (Wood shake treated with CCA)	2	803-1,063	< LOD	653 - 783	3,933-4,715	< LOD	< LOD	< LOD
WOS (Wood shingle)	1	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
GST (Glass at steep slope)	2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Low-Slope Panels								
BUA (modified built-up roof with APP cap sheet)	3	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
BUR (built-up roof with oxidized asphalt cap sheet)	2	< LOD	< LOD	< LOD	< LOD	< LOD-18	< LOD	< LOD
BUS (modified built-up roof with SBS cap sheet)	2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
EPD (Ethylene propylene diene monomer, EPDM)	2	7-10	< LOD	< LOD	< LOD	< LOD	4,151-6,449	< LOD
PVC (Polyvinyl chloride)	2	< LOD-100	< LOD	< LOD	< LOD	< LOD	208-270	< LOD
TPO (Thermoplastic polyolefin)	2	< LOD	< LOD	< LOD	< LOD	< LOD	11-477	< LOD
ZIN (Zincalume®)	2	NM	517-696	< LOD	< LOD	< LOD	513,309-521,787	< LOD-45
GLO (Glass at low slope)	2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

LOD: Limit of detection
NM: Not monitored by XRF unit due to unit error

Pilot-Scale Runoff Analysis

Summarized results from this pilot-scale roof runoff study are provided in the subsequent subsections. Appendix C provides the rain gage data for the sampling season and the field notes. Appendix D provides data tables for the analytical data. Appendix E provides copies of the laboratory data in pdf format. Validated analytical results for each rain event are available in Excel format upon request as Appendix F.

Throughout this and subsequent sections of the report, roofing panels are referred to by their abbreviations as provided in Table 2. Where summary data are provided, they are listed in alphabetical order by abbreviation for steep-slope panels and low-slope panels separately, with the glass control panels listed last in each category.

Observations of post-installation decontamination and rain events that may be pertinent to the understanding of the results include the following:

- During decontamination with the tap water, Ecology's project lead noted that unless the garden hose delivering the tap water was directed specifically perpendicular to the long edge of the panels, water did not flow off the sides of the panels. This was true for both the steep-slope and low-slope panels, specifically including the low-slope glass control panel. This observation indicates that rain flowed down the long access of the panels and into the gutters, unless exposed to high cross winds.
- Precipitation did not come into observable contact with the materials underlying the roofing materials, except initially for the concrete tile roof. As installed, the lowest row of tiles on the concrete tile roof (i.e., those closest to the gutter) allowed water to wick back up under the tiles contacting the underlying plywood and bypassing the gutter. This was remedied prior to the first runoff sample collection, by raising this row by approximately one centimeter. The minor modification ensured that the rain dropped freely from the tile into the gutter.
- Observations of all roofs as installed indicated that the down slope edges of the materials were exposed to precipitation, per standard installation.
- Installation of the single-ply and built-up roofs included a flap of the roofing material that extended from the upper surface approximately 2.5 cm into the gutter. Water from these roofs flowed over the flap of roofing material and into the gutter, lengthening the flow path by less than 2%.

Rain Events

Table 9 shows the range of rain event data including precipitation amount, duration, peak and average intensities, wind speed, and direction. Tables in Appendix D provide the weather-related data for each rain event in English and metric units, respectively. Metric units will be used hereafter in this report. Rain data were obtained from the tipping bucket rain gage co-located with roofing panels.

Table 9. Ranges of rain event data in metric units.

Metric	**Ranges**
Rain event date(s)	2/21 - 4/19/2013
Rain event duration (hrs) [a]	2.75 - 23.25
Precipitation in 6 hours preceding event (mm)[b]	0.0 - 2.3
Hours preceding event with no measurable precipitation[b]	0.0 - 31.5
Total precipitation (mm)[b]	4.3 - 18.8
Average rain intensity (mm/hr.)[b]	0.3 - 3.7
Average rain intensity when rain falling (mm/hr.)[b]	1.17 - 3.7
Peak rain intensity (mm/15 min.)[b]	0.51 - 1.5
Minimum rain intensity (mm/15 min.)[b]	0.0 - 0.25
Average wind speed during event (km/hr)[c]	0.2 - 6.2
Highest wind gusts (km/hr.)[c]	3 - 17
Average wind direction during event (^{o})[c]	175 - 310
Average wind direction when rain falling (^{o})[c]	68 - 204
Average temperature (^{o}C)[d]	4.6 - 11.4
Low temperature (^{o}C)[d]	2.0 - 10.6
High temperature (^{o}C)[d]	6.0 - 13.3

a Rain event duration = (Event stop time and date) - (event start time and time).
b Data from tipping bucket rain gage co-located with roofing panels at the Department of Ecology, Lacey, Washington.
c Wind speed and direction data obtained from Weather Underground (www.wunderground.com) station KWALACEY6.
d Temperature data obtained from Olympia Airport (MesoWest: http://mesowest.utah.edu/cgi-bin/droman/mesomap.cgi?state=WA&rawsflag=3).

The event duration was calculated from the beginning of the rain until the gutters were removed or the rain stopped, whichever was shorter. For some events, gutters were placed after the rain had begun. For other events, the gutters and collection containers were placed prior to the beginning of the event. For three events (Events 1, 6, and 8), the gutters were removed to stop the rain event and begin sampling. For the remainder of the events, there was at least a half hour lull in the rain event after the gutters were removed. Table 9 gives the range of antecedent rain conditions.

The sampled events represented a range of precipitation amounts for those events that provided sufficient rainfall to sample throughout the sampling season, as depicted in Figure 2. The cumulative rainfall between January 29, 2013 (when panel installation and decontamination were complete) and April 19, 2013 (the final sampling event) was 313.2 mm. Of this amount, a total of 106.2 mm, or 34% of the rainfall, was collected for sampling. Figure 3 shows the distribution of the events by rainfall amount.

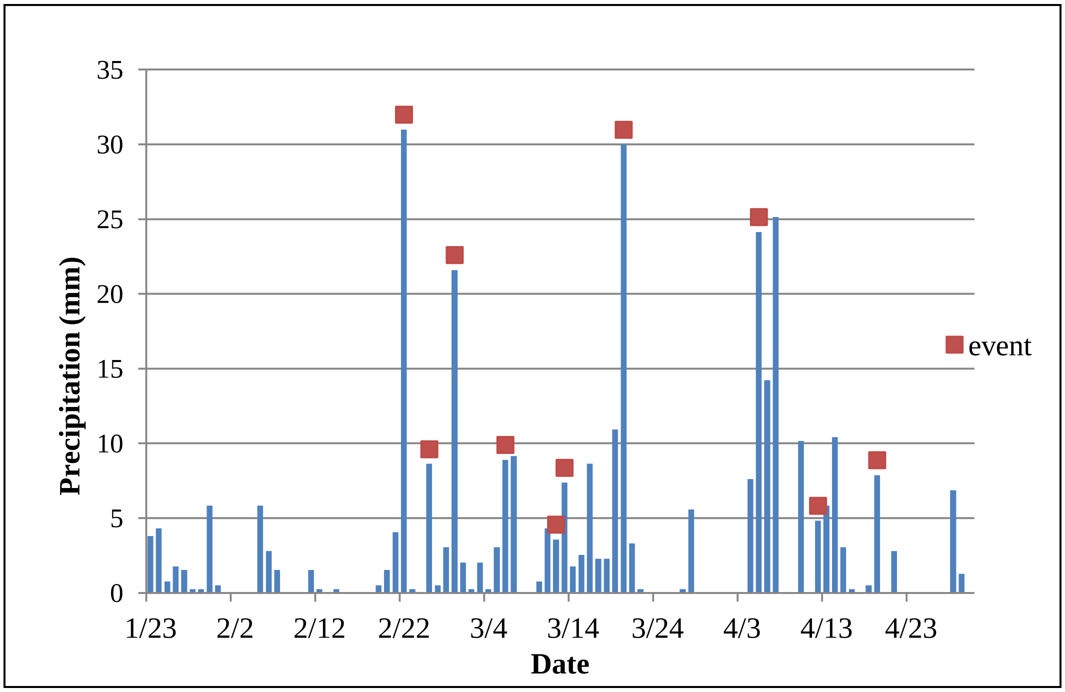

Figure 2. Hyetograph of precipitation over the sampling season with sample dates marked (red squares).

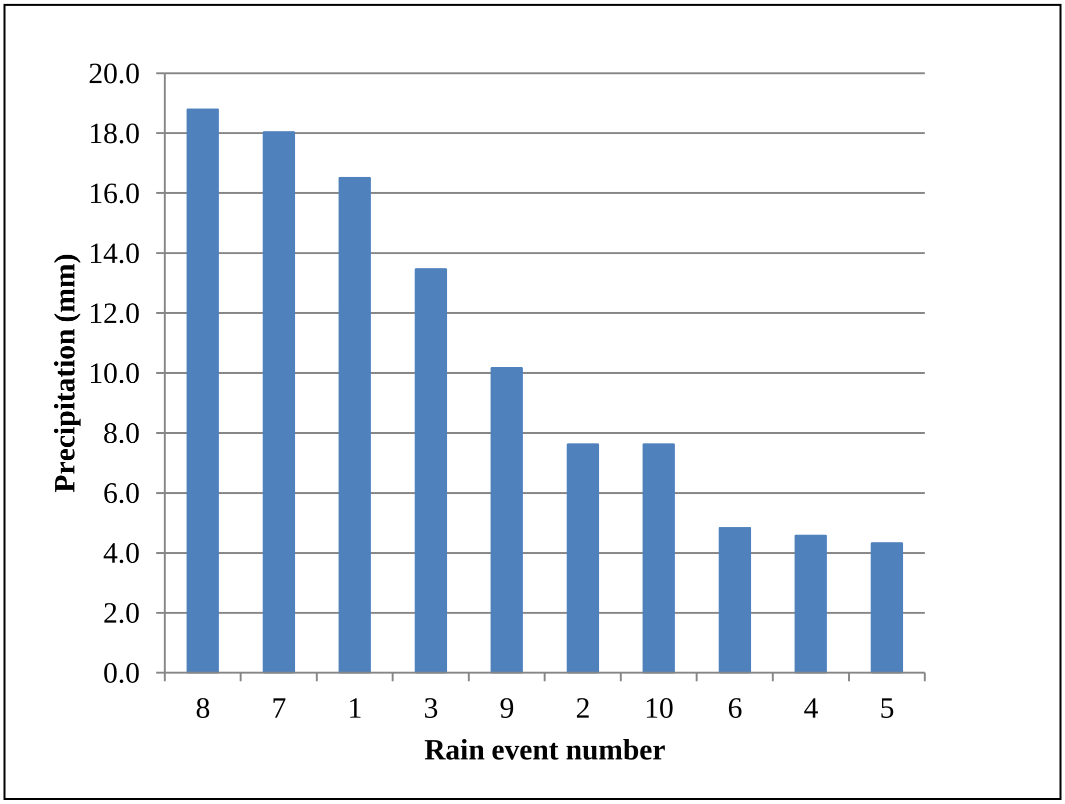

Figure 3. Distribution of rainfall amounts for sampled events (by event number).

Table 9 indicates that the average rain intensities (rain depth divided by rain event duration) ranged from 0.28 to 3.7 mm/hr. Because some rain events included one or more 15-minute intervals without measurable amounts of rain, an average intensity was also calculated for those intervals when at least 0.25 mm of rain fell; these ranged from 1.17 to 3.7 mm/hr. These values (average intensity when rain was falling) were calculated by dividing the total rainfall by the number of 15-minute intervals in which rain was recorded in the tipping bucket rain gage (divided by 4 to convert to hours).

Wind direction and speed were obtained from weather station KWALACEY6, a private weather station in Lacey, Washington accessed through the Weather Underground website (Weather Underground, 2013). The weather station was selected for its close proximity to the study location (one mile to the west) and the completeness of the data set. Ecology has an air quality monitoring station two miles to the south as a part of air quality monitoring program, but it was not operational during the time sampling occurred.

KWALACEY6 weather data were recorded in 5-minute intervals, which were averaged into 15- minute intervals to match the 15-minute precipitation data collected at the study location. Ecology calculated the average wind speeds and directions using vectors. The wind speed represented magnitude of the vector, and the direction represented the orientation. These two values were converted into radians and multiplied for each 15-minute interval. The vectors were then broken down into their x and y components. All x components and y components were separately averaged for all 15-minute data for each event. The event average speed and direction were calculated from the average x and y values for an event using the Pythagorean Theorem and arctangents of y/x. Average wind speeds ranged from 0.2 to 6.2 km/hr, while gusts ranged from 5 to 26 km/hr. Six of the 10 events were within 20^o of the prevailing wind direction.

Average minimum and maximum temperature data were obtained from the Olympia Airport. Ambient temperatures gradually increased with the coming of spring.

The nearest station measuring concentrations of sulfur dioxide was the Seattle Beacon Hill station. During the course of the study, sulfur dioxide concentrations at that station ranged from 0.3 to 5.0 ppb, averaging 0.7 ppb (Puget Sound Clean Air Agency, 2013). These concentrations are well below thresholds which might result in greater release of pH-sensitive constituents such as metals.

Field Data

Table 10 shows summary statistics for pH, temperature, and specific conductance across rain events. The median pH values do not include data taken from Event 9 (April 11, 2013) because the pH meter was not functioning properly and continued to drift. The pH values for the glass control panels do not necessarily reflect the pH of the rain, because pH may vary with holding time (holding time includes the length of the event and the length of time until each roof was sampled). Both pH and specific conductance reflect the composition of the roofs and length of exposure to the rain as well as initial composition of the rain itself.

Table 10. Summary of field parameters by roofing type for 10 rain events.

Field Parameter	**Steep-Slope Panels**								**Low-Slope Panels**							
	AAR	**AS[A]**	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**	**GST**	**BUA**	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
pH[a]																
Median	6.6	6. 8	5.9	7.8	4.9	4.7	3.8	4.8	6.1	6.6	7.1	4. 6	5.0	5.8	5.2	5.0
Minimum	5.9	4.8	4.9	7.0	4.3	4.3	3.5	4.5	5.3	5.8	5.3	4.2	5.6	4.6	4.1	4.6
Maximum	8.1	7.1	7.1	9.1	6.2	5.1	5.6	6.3	7.1	7.2	7.4	5.0	5.2	5.2	5.9	6.8
Temperature (^{o}C)																
Median	6.0	6.6	6.8	5.9	7.2	6.2	6.6	6.2	5.3	6.4	5.4	6.2	6.3	6.8	7.0	6.0
Minimum	3.2	3.1	2.5	1.8	2.9	3.2	2.7	1.6	1.0	2.4	2.8	1.9	1.4	2.0	2.6	1.7
Maximum	10.9	11.6	11.0	11.4	11.2	11.4	11.5	11.0	10.2	10.6	10.9	11.3	11.2	11.7	10.9	11.5
Specific Conductance (us/cm)																
Median	11	11	4	62	5	12	80	2	4	9	8	9	3	3	3	1
Minimum	3	3	0	18	0	2	32	0	0	1	0	1	0	0	0	0
Maximum	21	26	11	116	16	24	175	10	11	25	16	25	16	13	41	17

[a] Event 9 pH data not included in median due to pH meter drift.
[A] Average of three replicate asphalt shingle panels (AS-1, AS-2, and AS-3).
Shading indicates glass control panels.
Panel identification codes are defined in Table 2 on page 40.

Temperatures were more reflective of the ability of the ice baths to maintain low temperatures than the ambient conditions with the coming of spring. The maximum sample temperatures were all measured during Event 10. Appendix C provides the complete data set for these parameters. Variations in the pH values, conductivities, and temperatures for a panel type may have been a function of the length of the rain event and also the length of time from the end of the rain event until the sample was measured.

Ecology measured the volume of runoff recovered in each stainless-steel container for each rain event. The ranges of collected volumes are provided in Table 11. The volumes measured per event for each panel are provided in Appendix D. The volume collected compared to the theoretical volume that fell on each panel will be discussed later.

Table 11. Summary statistics of volume of runoff collected for each rain event.

Event #	**Total Precipitation (mm)**	**Volume Collected (L)**		
		Minimum	**Median**	**Maximum**
1	16.51	51.6	56.3	65.5
2	7.61	20.9	24.8	26.8
3	13.46	33.3	39.2	42.7
4	4.57	9.9	12.9	13.9
5	4.31	12.4	16.6	18.9
6	5.08	10.9	16.6	17.9
7	18.03	33.8	44.7	48.7
8	18.80	43.7	56.9	59.6
9	10.16	25.3	27.8	29.8
10	7.61	18.9	22.8	25.8

Total Metals

Total metals concentrations were analyzed for each rain event. The concentrations of total metals measured are presented in Appendix D for arsenic, cadmium, copper, lead, and zinc.

Figures 4 through 8 depict the concentrations graphically for arsenic, cadmium, copper, lead, and zinc, respectively. Note that the concentrations (y axis) on these graphs are displayed on a log scale. The roofing panels are identified along the x axis as defined in Table 2 and throughout the report. A blue vertical bar is used to depict the values at half of the MDL, when no metals were detected in the sample. In Figures 4 through 8, AS represents the average of the three replicate asphalt shingle panels.

Ecology created Figures 4 though 8 using R version 2.15.2 and ggplot version 0.9.3 (R Core Team, 2012; Wickham, 2009). These ggplots serve two useful purposes. First, where an analyte was not frequently detected, the vertical bars provide a quick visual indicator of the frequency of non-detections. Cadmium results (Figure 5) provide the best example of where no cadmium was detected in many of the samples. The detection frequency for cadmium was only 33%, where the detection frequencies for copper and zinc were 100%. The detection frequencies for arsenic and lead were also high at 90 and 99%, respectively. The second purpose of the ggplots is that one can easily compare the runoff quality from glass control panels (GST and GLO for steep- and low-slope panels, respectively) with those of the other panels to get a visual understanding of differences in runoff concentrations. Total metals will be discussed in greater detail in the *Discussion* section of this report.

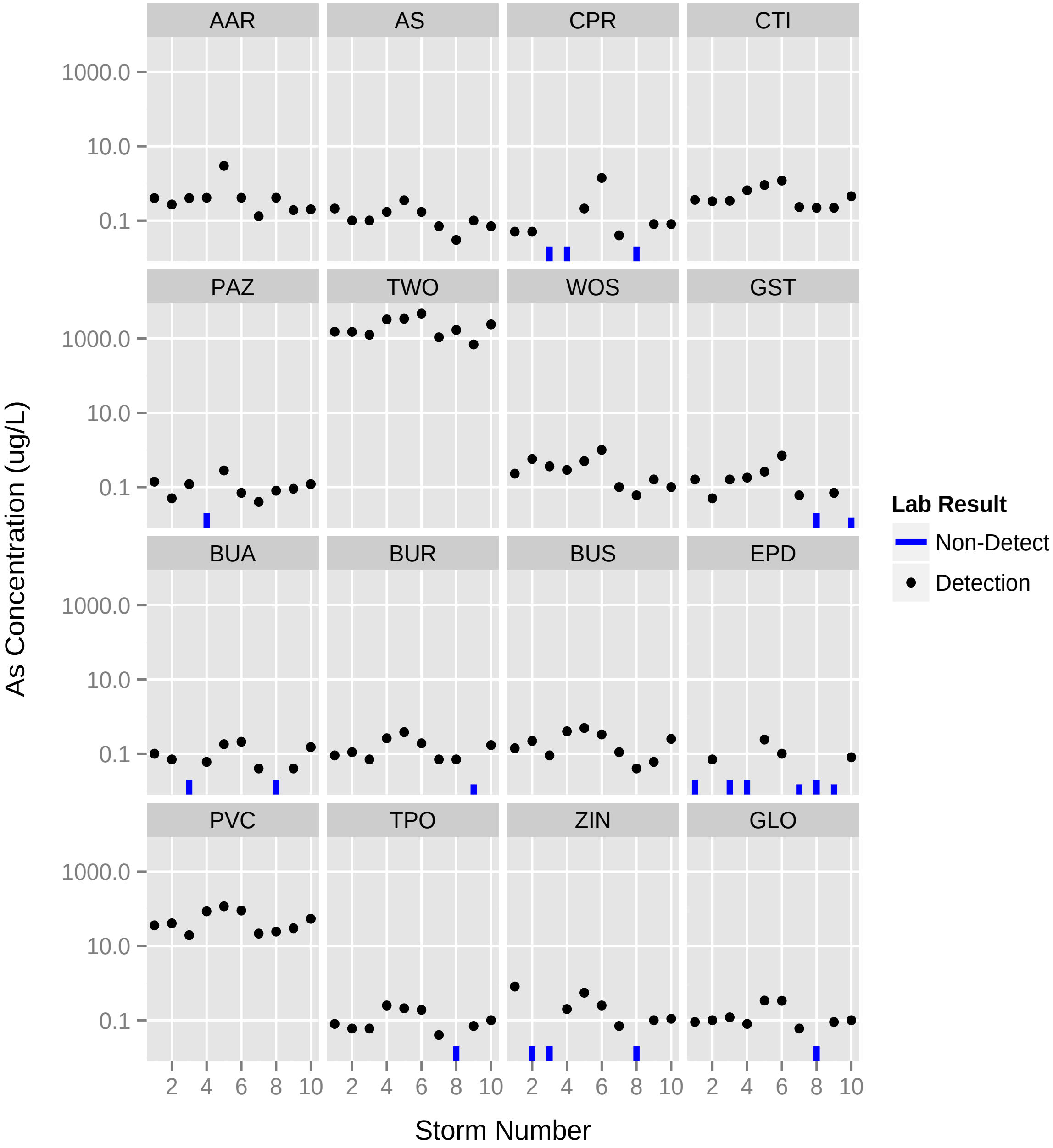

Figure 4. Total arsenic concentrations in runoff by panel and event (storm) number. Panel identification codes are defined in Table 2 on page 40.

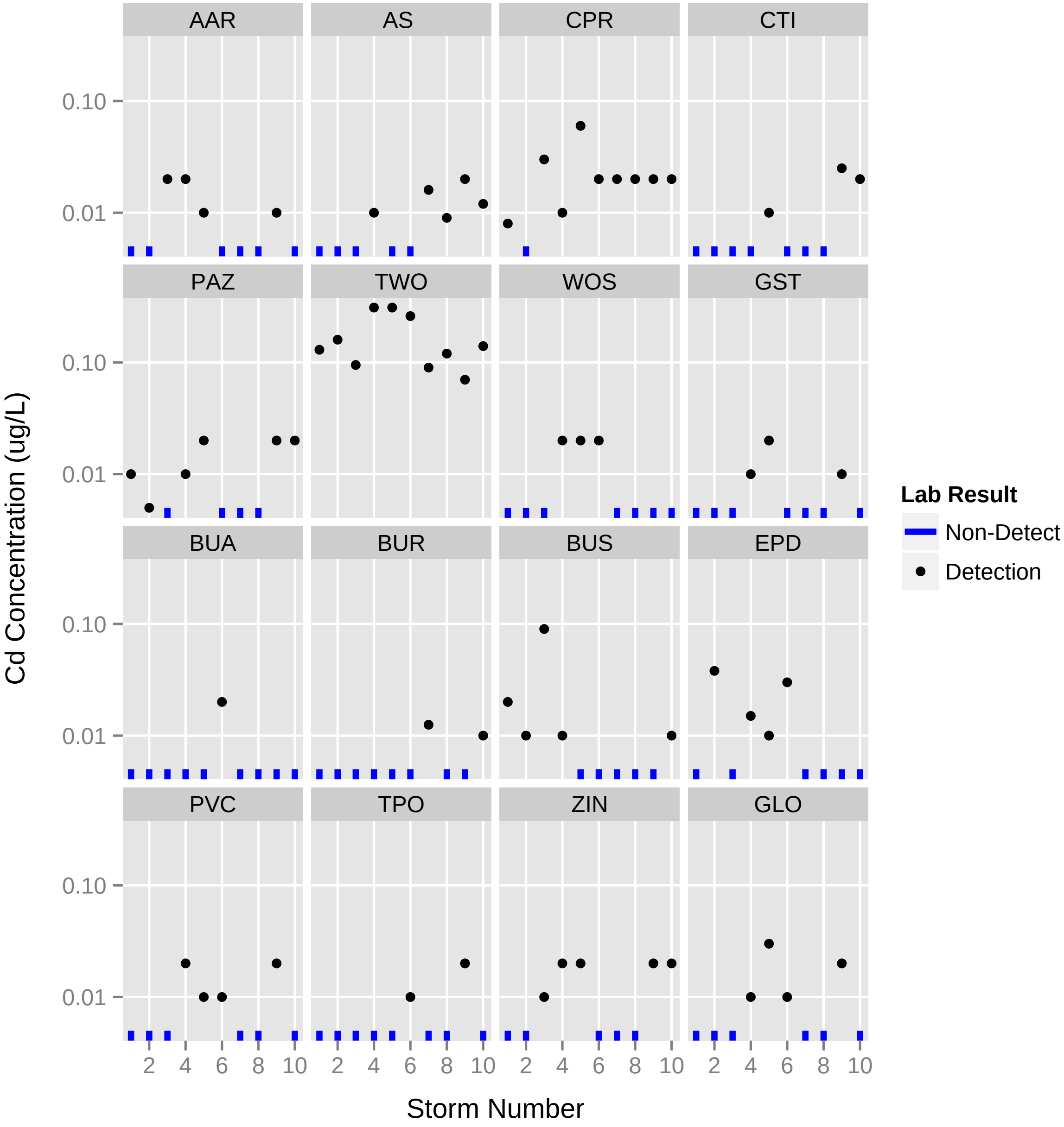

Figure 5. Total cadmium concentrations in runoff by panel and event (storm) number. Panel identification codes are defined in Table 2 on page 40.

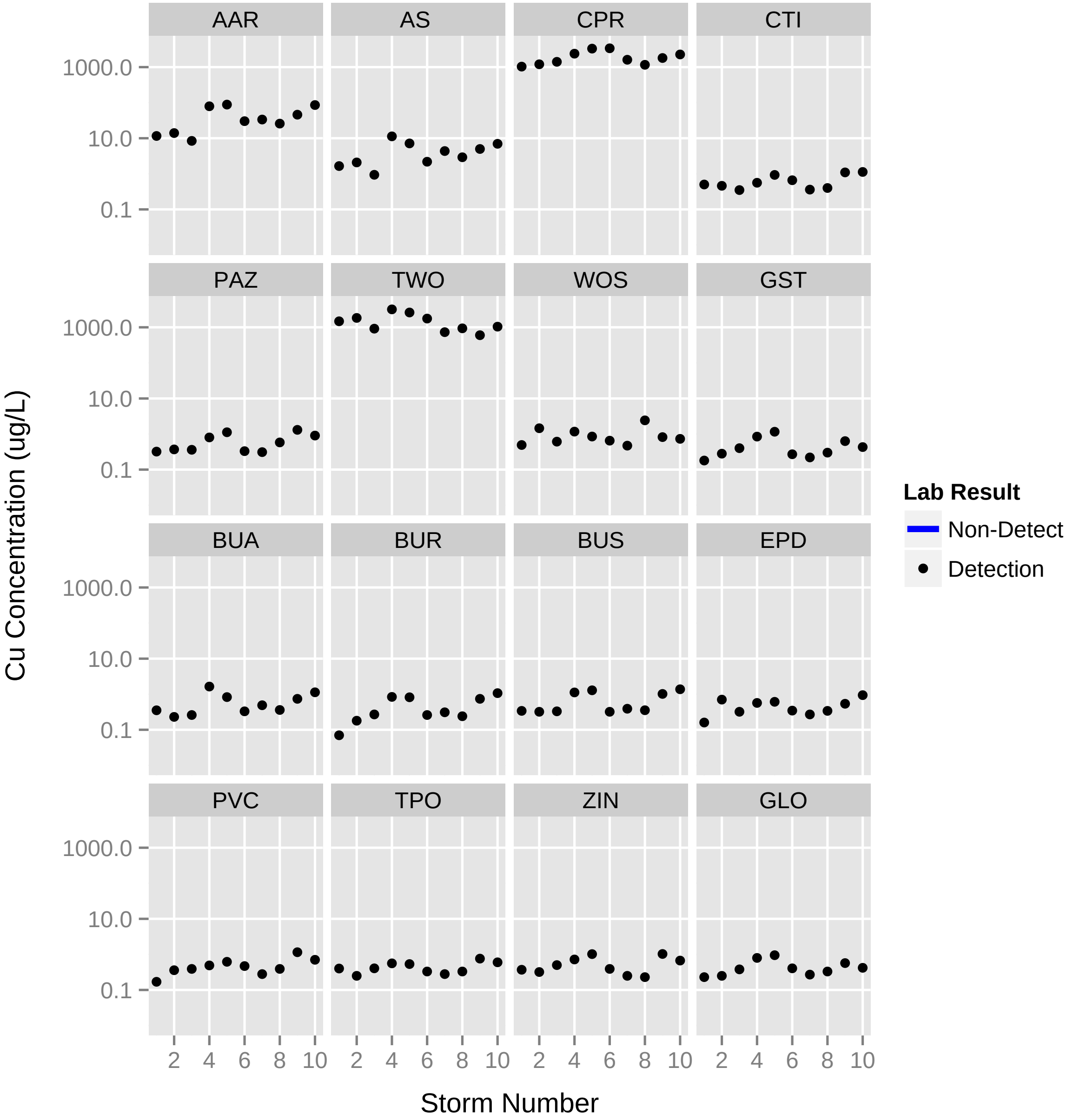

Figure 6. Total copper concentrations in runoff by panel and event (storm) number.
Panel identification codes are defined in Table 2 on page 40.

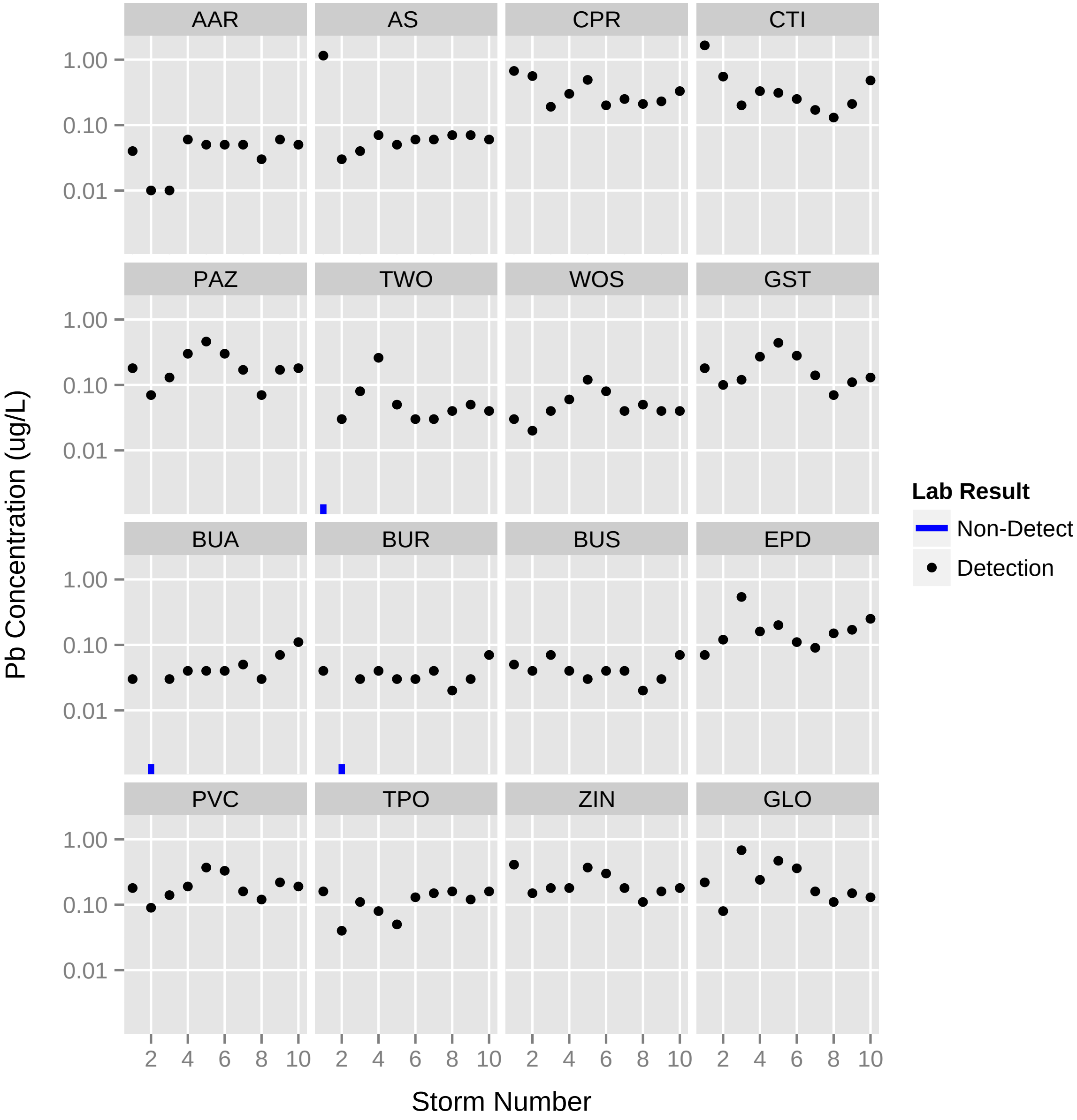

Figure 7. Total lead concentrations in runoff by panel and event (storm) number. Panel identification codes are defined in Table 2 on page 40.

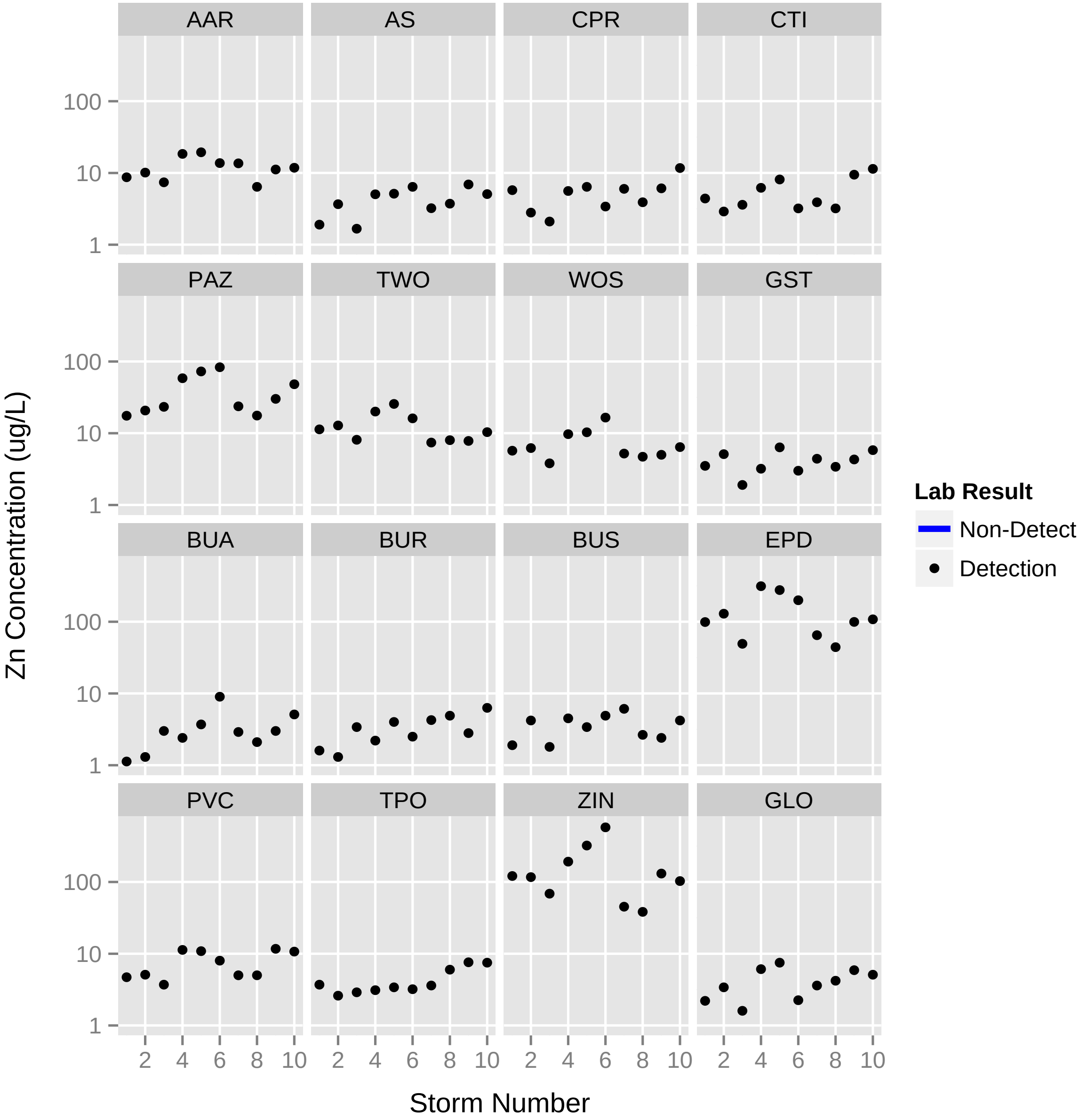

Figure 8. Total zinc concentrations in runoff by panel and event (storm) number. Panel identification codes are defined in Table 2 on page 40.

Dissolved Metals

Dissolved metals concentrations were analyzed for the first three rain events. All of these data were qualified as estimates "J" flag, because the samples were not filtered and preserved within the EPA-specified 15-minute holding time. Tables in Appendix D provide the concentrations of dissolved arsenic, cadmium, copper, lead, and zinc. Consistent relationships between dissolved and total metals concentrations by panel type were discernible only for those metals that were substantially higher than the MDLs. In some instances, the dissolved fraction was substantially higher than the total fraction (i.e., substantially greater than 100%). This is likely due to different laboratory sensitivities and other factors that will be discussed subsequently.

PAHs

Ecology sampled runoff from all panels for PAHs for the first three rain events. Thereafter, staff sampled for PAHs on asphalt-based (AAR, AS^A, BUA, BUR, and BUS), the single-ply, and the glass control panels.

PAHs detected across all 10 rain events above a concentration 5 times the contamination in the method or equipment rinse blanks are presented in Table 12. A concentration 5 times the concentration found in the method blank is defined as the laboratory contaminant threshold, while a concentration 5 times the contamination found in the equipment rinse blank is defined as the equipment blank contaminant threshold (Ecology, 2013a).

The numbers in Table 12 represent the number of rain events that a compound was detected on a particular panel (Appendix D provides data tables.). Phenanthrene was detected most frequently in runoff from the roof panels. Naphthalene and pyrene had less than half of the number of detections that phenanthrene did. As evidenced from Table 12, four of the 18 monitored PAHs [acenaphthene, acenaphthylene, benz(a) anthracene, and dibenzo(a,h,) anthracene] were not detected in the runoff from any panel above the laboratory contaminant threshold.

The specific PAH compounds detected and their concentrations exhibited great spatial variability. For example, results from the three replicate asphalt shingle panels (AS^A) in Event 1 provide an example. These panels are located on approximately three-meter centers. The laboratory reported six PAH compounds in the runoff from AS-1, one PAH compound from AS-2, and two from AS-3. Further, the split sample for AS-1 had only two PAH detections. Similar spatial variability exists between the glass control panels located approximately six meters apart. Again for Event 1, runoff from the low-slope glass control panel included four PAH compounds, while runoff from the steep-slope glass control panel included three compounds, two of which differed from those detected on the low-slope glass panel.

To assess the overarching results of the PAH analyses and reduce the impacts of low concentrations of various compounds, Ecology calculated the sums of the detected PAH compounds for each panel and each rain event. The sums of the detected PAH concentrations for each panel and each rain event are presented in Table 13. The significance of these data will be assessed in the *Discussion* section.

Table 12. PAH compounds detected above laboratory and equipment contamination thresholds for all 10 rain events.

Compound	Steep-Slope Panels								Low-Slope Panels							
	AAR	**AS**[A]	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**	**GST**	**BUA**	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
1-Methylnaphthalene		3				3		1		1	7	1	1			
2-Methylnaphthalene	2	3	1				1	1		1	7	1			1	2
Acenaphthene																
Acenaphthylene																
Anthracene		1			1			2	1		1		1	1		2
Benz[a]anthracene																
Benzo(a)pyrene		1	2	1				3	1			1		1		4
Benzo(b)fluoranthene		2	2	2	2			2				3	2	3	1	3
Benzo(ghi)perylene		2	1	1	1			3				6	1	1	2	2
Benzo(k)fluoranthene		2	1	2	2			2				2	1	1	1	3
Chrysene	1	3		1	1				1					1		
Dibenzo(a,h)anthracene																
Fluoranthene			1		1	1		1	1		1	8	2	1	2	5
Fluorene	1	4			1			1		2	4					
Indeno(1,2,3-cd)pyrene		1	1		1		1	2				2	1	2	2	2
Naphthalene	1	3	1	1	1	1		2	1	2	7	1		2	1	3
Phenanthrene	8	10	2	3	3			7	6	9	10	4	2	5	3	5
Pyrene	1	1	2	2	2			4	1		2	10	2	2	2	4

[A] Average of three asphalt shingle panel replicates.
Shading indicates glass control panels.
Panel identification codes are defined in Table 2 on page 40.

Table 13. The sum of detected PAHs (in ug/L) by panel and event number.

Event #	Total Precip. (mm)	Steep-Slope Panels																Low-Slope Panels															
		AAR		AS[A]		CPR		CTI		PAZ		TWO		WOS		GST		BUA		BUR		BUS		EPD		PVC		TPO		ZIN		GLO	
1	16.5	**0.012**		**0.023**	J,a	**0.012**	J,a*	**0.040**	J	**0.022**	J	**0.016**	J	**0.130**	J	**0.016**	J	**0.013**	J,a	**0.010**	J	**0.029**	J	**0.073**	J	**0.010**	J	**0.061**	J	**0.027**	J	**0.029**	J
2	7.6	**0.010**	J	**0.039**	J,*	**0.051**	J	**0.025**	J	**0.037**	J,a*	**0.027**	J	**0.011**	J	**0.065**	J,a*	**0.005**	J	**0.017**	J	**0.057**	J	**0.088**	J,a*	**0.036**	J	**0.016**	J	**0.049**	J	**0.065**	J
3	13.5	**0.032**	J,a	**0.040**	J,*	**0.051**	J	**0.033**	J	**0.048**	J	**0.060**	J,a*	**0.048**		**0.032**	J	**0.036**	J	**0.037**	J	**0.116**	J	**0.069**		**ND**		**0.022**	J,a*	**0.029**	J	**0.041**	J
4	4.6	**0.018**		**0.015**		-		-		-		-		-		**0.039**	J,a*	**0.010**	J	ND		**0.132**	J	**0.086**	J,a*	**0.030**	J	**0.007**	J	-		**0.041**	J,a*
5	4.3	**0.020**		**0.020**	J	-		-		-		-		-		**0.066**	J,a	L		**0.019**	J	**0.126**		**0.103**		ND	a	**0.011**	J,a*	-		**0.036**	J
6	5.1	**0.021**	J	**0.024**	J,a*	-		-		-		-		-		**0.022**	J	**0.009**	J	**0.014**	J	**0.083**	J	**0.084**	J,a*	**0.005**	J	**0.008**	J	-		**0.023**	J,a
7	18.0	**0.013**	J	**0.019**	J,a*	-		-		-		-		-		**0.018**	J	ND		**0.013**	J,a	**0.093**	J	**0.041**	J	ND		ND		-		**0.020**	J
8	18.8	**0.011**		**0.011**	J,a*	-		-		-		-		-		ND		ND		**0.011**		**0.054**	J,a*	**0.069**	J	ND		ND		-		ND	
9	10.2	**0.005**	J,a*	**0.021**	J,a*	-		-		-		-		-		**0.087**	J	ND	a	**0.011**		**0.032**	J	**0.083**		**0.039**	J	**0.008**	J	-		**0.069**	J
10	7.60	**0.024**	J	**0.023**	J	-		-		-		-		-		ND		**0.008**	J	**0.013**	J,a	**0.029**		**0.051**	J	ND		ND	a	-		ND	

[A] Average of three replicate asphalt shingle panels
[a] Average of split samples
J: Value is an estimate
L: Sample lost
ND: Analyte not detected at the method detection limit (MDL).
* In summing, values detected above MDL in one replicate were averaged with values at one-half the MDL in replicate for the same compounds in replicate that were not detected.
Bold: analyte detected above the MDL.
Shading indicates glass control panels.
Panel identification codes are defined in Table 2 on page 40.

Phthalates

Ecology sampled runoff from all panels for phthalates for the first three rain events. Thereafter, staff sampled for phthalates on the asphalt-based, the single-ply, and the glass control roofing panels.

Concentrations of detected phthalates were low across all panels. Those phthalates detected above the laboratory contaminant threshold are listed by panel in Table 14. Those panels not depicted in Table 14 did not have phthalates detected in the runoff from any rain event. The numbers in Table 14 represent the number of rain events that a compound was detected on a particular roof type (Appendix D provides data tables.) Di-N-butylphthalate was not detected in any rain event. Di-N-octylphthalate was detected on the greatest number of roofs. The treated wood shake roof was the only roof type that had three detections of phthalates, and in each of the three rain events bis (2-ethylhexyl) phthalate was detected.

Table 14. Phthalates detected at concentrations greater than 5 times the method blanks.

Compound	**Steep-Slope Panels**					**Low-Slope Panels**					
	AS[A]	**CPR**	**PAZ**	**TWO**	**WOS**	**BUA**	**BUR**	**BUS**	**EPD**	**PVC**	**GLO**
Bis(2-ethylhexyl) phthalate	1	1		3	1						
Benzyl butylphthalate	2										
Diethyl phthalate			1								2
Dimethyl phthalate				1							1
Di-N-butylphthalate											
Di-N-octylphthalate	2	1		1		1	1	1	1	1	2

[A] Average of three replicate asphalt shingle panels.
Shading indicates glass control panel.
Panel identification codes are defined in Table 2 on page 40.

To assess the overarching results of the phthalate analyses and reduce the impacts of low concentrations and laboratory contamination, Ecology calculated the sums of the phthalates compounds for each panel and each rain event. These are presented in Table 15. Phthalates will be further assessed in the *Discussion* section.

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Table 15. The sum of detected phthalates (in ug/L) by panel and event number.

Event #	Total Precip. (mm)	Steep-Slope Panels																Low-Slope Panels																	
		AAR		**AS**^{A}		**CPR**		**CTI**		**PAZ**		**TWO**		**WOS**		**GST**		**BUA**		**BUR**		**BUS**		**EPD**		**PVC**		**TPO**		**ZIN**		**GLO**	
1	16.5	ND		**0.64**	J,a*	**0.57**	J,a	ND	a	ND		**4.60**	J	ND		ND		ND	a	ND		ND		ND		**0.440**	J	ND		ND		**0.20**	J
2	7.6	ND		**0.22**	J	ND		ND		**0.02**	J,a*	**4.20**	J	**0.85**	J	ND	a	ND		ND		ND		ND	a	ND		ND		ND		ND	
3	13.5	ND	a	ND		ND		ND		ND		**1.82**	J,a*	ND		ND		**0.25**	J	ND		ND		**0.32**	J	ND		ND	a	ND		**0.53**	J
4	4.6	ND		ND		-		-		-		-		-		ND	a	ND		ND		ND		**0.12**	J,a	ND		ND		-		**0.43**	J,a*
5	4.3	ND		ND		-		-		-		-		-		ND	a	L		ND		ND		ND		ND	a	ND	a	-		**0.13**	
6	5.1	ND		ND		-		-		-		-		-		ND		ND		ND		ND		ND	a	ND		ND		-		ND	a
7	18.0	ND		ND	a	-		-		-		-		-		ND		ND		ND	a	ND		ND		ND		ND		-		ND	
8	18.8	ND		ND	a	-		-		-		-		-		ND		ND		ND		ND	a	ND		ND		ND		-		ND	
9	10.2	ND	a	ND	a	-		-		-		-		-		ND		ND	a	**0.2**	J	**0.2**	J	ND		ND		ND		-		ND	
10	7.60	ND		ND		-		-		-		-		-		ND		ND		ND	a	ND		ND		ND	a	ND	a	-		ND	

^{A} Average of three replicate asphalt shingle panels
^{a} Average of split samples
J: Value is an estimate
L: Sample lost
ND: Analyte not detected at MDL
* In summing, values detected above MDL in one replicate were averaged with values at one-half the MDL in replicate for the same compounds in replicate that were not detected.
Bold: analyte detected above the MDL.
Shading indicates glass control panels.
Panel identification codes are defined in Table 2 on page 40.

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PBDEs

PBDEs were analyzed in runoff from all panels for the first three rain events. Thereafter PBDEs were measured only in runoff from the single-ply and the two glass control panels.

PBDE congeners were rarely detected and only at concentrations between the MDL and the reporting limit (RL), except two detections in Event 1 that were above the RL on the copper (CPR) and wood shingle (WOS) panels. See data tables in Appendix D. Table 16 identifies the congeners detected by roof type and the rain event in which they were detected. PBDE-099 was detected most frequently, and congener -184 was detected least frequently. PBDE-153 was not detected in any rain event in runoff from any roof type.

Table 16. PBDE congeners detected by panel and number of rain events in which detected.

Congener	**Steep-Slope Panels**				**Low-Slope Panels**			
	CPR	**TWO**	**WOS**	**GST**	**EPD**	**PVC**	**TPO**	**GLO**
PBDE - 049		3						
PBDE - 099	1		1,2,3	4	4		1,2,4	4
PBDE - 100	1		1	4				4
PBDE - 153								
PBDE - 154	1	3						
PBDE - 183					1,3			4
PBDE - 184						5		
PBDE - 191		3	3					
PBDE - 209							1,2	

Shading indicates glass control panels.
Panel identification codes are defined in Table 2 on page 40.

Because concentrations were low and infrequent, the sums of the PBDE congeners are presented in Table 17 for the steep-slope panels and Table 18 for the low-slope panels. The sum was calculated by adding concentrations that were either J flagged as estimates or were reported above the RL.

Table 17. The sum of detected PBDE congeners (in ug/L) for steep-slope panels for all rain events.

Event #	**Total Precip (mm)**	**Steep-Slope Panels**											
		AAR	**AS**[A]	**CPR**		**CTI**	**PAZ**	**TWO**		**WOS**		**GST**	
1	16.5	ND	ND	**0.004**	J,a*	ND	ND	ND		**0.005**	J,a	ND	
2	7.6	ND	ND	ND		ND	ND	ND		**0.003**	J	ND	a
3	13.5	ND	ND	ND		ND	ND	**0.003**	J,a*	**0.004**	J	ND	
4	4.6	--	--	--		--	--	--		--		**0.001**	J,a*
5	4.3	--	--	--		--	--	--		--		ND	a
6	5.1	--	--	--		--	--	--		--		ND	
7	18.0	--	--	--		--	--	--		--		ND	
8	18.8	--	--	--		--	--	--		--		ND	
9	10.2	--	--	--		--	--	--		--		ND	
10	7.60	--	--	--		--	--	--		--		ND	

[A] Based on average of three replicate asphalt shingle panels

[a] Based on average of split samples

J: Estimated values between the MDL and RL included

* In summing, values detected above the MDL in one replicate were averaged with values at one-half the MDL in replicate for the same compounds in replicate that were not detected.

ND: Congener not detected at the MDL

- Not sampled

Shading indicates glass control panels

Panel identification codes are defined in Table 2 on page 40.

Table 18. The sum of detected PBDE congeners (in ug/L) for low-slope panels for all rain events.

Event #	Total Precip (mm)	Low-Slope Panels											
		BUA	**BUR**	**BUS**	**EPD**		**PVC**		**TPO**		**ZIN**	**GLO**	
1	16.5	ND	ND	ND	**0.002**	J	ND		**0.005**	J	ND	ND	
2	7.6	ND	ND	ND	ND	a	ND		**0.002**		ND	ND	
3	13.5	ND	ND	ND	**0.002**	J	ND		ND	a	ND	ND	
4	4.6	--	--	--	**0.006**	J,a	ND		**0.005**	J	--	**0.002**	J,a
5	4.3	--	--	--	ND		**0.002**	J,a*	ND	a	--	ND	
6	5.1	--	--	--	ND	a	ND		ND		--	ND	A
7	18.0	--	--	--	ND		ND	a	ND		--	ND	A
8	18.8	--	--	--	ND		ND		ND		--	ND	
9	10.2	--	--	--	ND		ND		ND		--	ND	A
10	7.60	--	--	--	ND		ND	a	ND		--	ND	

[a] Based on average of split samples

J: Estimated values between the MDL and RL included

* In summing, values detected above MDL in one replicate were averaged with values at one-half the MDL in replicate for the same compounds in replicate that were not detected.

ND: Congener not detected at the MDL

- Not sampled

Shading indicates glass control panels

Panel identification codes are defined in Table 2 on page 40.

SPLP Analysis

The laboratory exposed each of the three replicates of each coupon (with or without coating) to 1.7 liters of synthetic precipitation for 18 to 20 hours. The coupons were tumbled during this period. The leachate was filtered and analyzed for five metals (arsenic, cadmium, copper, lead, and zinc). For replicates -01 and -02, the method blanks were highly contaminated with zinc that was associated with the filter. The process was repeated without filtration for the metals analyses. Replicate -03 was leached the first time and was not filtered. It was also leached a second time to parallel the treatment of the first two replicates. Data for metals from both leachings are provided in tables in Appendix D. This second round of leaching was not described in the QA Project Plan (Ecology, 2013a), but was necessary because the first leaching was so highly contaminated with zinc from the filters that the data were not useful (56 ug/L of zinc in the -01 replicate and 34 ug/L of zinc in the -02 replicate). Data are available in Appendix F.

Metals

The objective of this portion of the study was to determine the effectiveness of the coatings at preventing either total copper or total zinc from leaching into the synthetic precipitation leachate. To assess effectiveness, staff only considered results of the second SPLP leaching. Table 19 presents the measured surface areas, coating weights, and zinc results for the zinc-based coupons, along with the percent reduction in zinc concentrations as a result of the coating.

Staff calculated percent reduction associated with the coating by dividing the concentration of zinc in the leachate from the coated coupon by the concentration of zinc in the leachate from the uncoated, galvanized steel coupon. Table 19 also shows the percent reduction of zinc leached from the Zincalume® compared to the galvanized steel coupons.

Table 19. Coating effectiveness at preventing zinc leaching from SPLP analysis.

Description	Coupon ID	Surface Area (mm^2)	Coating Weight (g)	Total Zinc (ug/L)	% Zinc Reduction
Zincalume®	ZIN-01	1,390	NA	394	62.1
	ZIN-02	1,390	NA	289	51.0
	ZIN-03	1,369	NA	345	53.3
Average % Zinc Reduction					**55.5[a]**
Galvanized steel	GAL-01	1,343	NA	1040	NA
	GAL-02	1,374	NA	590	NA
	GAL-03	1,306	NA	739	NA
Galvanized steel coated with Snow Seal™ (Ames Research Laboratories)	SNO-01	1,368	0.055	429	58.8
	SNO-02	1,402	0.050	375	36.4
	SNO-03	1,357	0.050	399	46.0
Average % Zinc Reduction					**47.1**
Galvanized steel coated with SHER-CRYL™ HPA High Performance Acrylic Semi-Gloss Coating (Sherwin Williams)	ASW-01	1,382	0.111	377	63.8
	ASW-02	1,307	0.077	247	58.1
	ASW-03	1,307	0.080	363	50.9
Average % Zinc Reduction					**57.6**
Galvanized steel coated with UNIFLEX® Elastomeric Roof Coating (Sherwin Williams)	ESW-01	1,327	0.173	182	82.5
	ESW-02	1,275	0.140	171	71.0
	ESW-03	1,281	0.152	59	92.1
Average % Zinc Reduction					**81.9**
Galvanized steel coated with Poly-Sil 2500 High Solids (Coatings & Foam Solutions)	SIL-01	1,335	0.281	545	47.6
	SIL-02	1,362	0.242	307	48.0
	SIL-03	1,328	0.219	280	62.1
Average % Zinc Reduction					**52.6**
Galvanized steel coated with Karnak® Fibered Aluminum Asphalt Coating 98AF	ALA-01	1,391	0.119	314	69.8
	ALA-02	1,357	0.108	373	36.8
	ALA-03	1,327	0.117	193	73.9
Average % Zinc Reduction					**60.2**
Galvanized steel coated with Quest Construction Products Elastuff™ 101	EPB-01	1,364	0.212	141	86.4
	EPB-02	1,311	0.229	5.3	99.1
	EPB-03	1,409	0.246	94	87.3
Average % Zinc Reduction					**91.0**

[a] This value represents the average difference between the leached zinc from the Zincalume® compared with the galvanized steel coupons.

Table 20 shows the same information for copper results from copper coupons. For the copper coupons, the manufacturer coated the coupons; thus, staff could not measure coating weights. Metals concentrations for arsenic, cadmium, and lead were low regardless of coupon or coating type.

Table 20. Coating effectiveness at preventing total copper leaching from SPLP analysis.

Description	Coupon ID	Surface Area (mm^2)	Coating Weight (g)	Total Copper (ug/L)	% Copper Reduction
Copper, uncoated	CUB-01	1,322	NA	383	NA
	CUB-02	1,398	NA	290	NA
	CUB-03	1,386	NA	365	NA
Copper coated with Syncrylac®	SYN-01	1,400	ND	101	73.6
	SYN-02	1,381	ND	83	71.5
	SYN-03	1,388	ND	103	71.8
Average % Copper Reduction					**72.3**
Copper coated with PPG Architectural Finishes Coraflon® ADS Intermix	COR-01	1,454	ND	183	52.2
	COR-02	1,386	ND	170	41.4
	COR-03	1,441	ND	113	69.0
Average % Copper Reduction					**54.2**

Organics

To determine whether coatings could leach organic contaminants, thereby exchanging release of one toxic compound for another toxic compound and not necessarily achieving environmental benefit, the laboratory analyzed PAHs, phthalates, and PBDEs in the leachate.

Table 21 shows the PAH compounds detected in the leachate from the coupons. Only those contaminants detected above the laboratory contaminant thresholds (i.e., 5 times the method blank concentration) are depicted. Coupons not listed in the table had no PAHs detected in the leachate above the method blank contaminant threshold. Thirty-seven percent of the detections were between the MDL and the RL. Data tables are in Appendix D.

The laboratory detected anthracene, fluorene, naphthalene, and pyrene on only one coupon. Both 1- and 2-methylnaphthalene were detected one or more times on all coupons, except those coated with Syncrylac® and Coraflon®. The Karnak® Fibered Aluminum Asphalt Coating, which is an asphalt-based coating, had the greatest number of PAH compounds detected.

Only one phthalate compound was detected above the laboratory contaminant threshold. The laboratory reported diethyl phthalate at 0.27 ug/L from one coupon coated with Elastuff™ 101.

The laboratory analyzed for PBDEs only on three replicates of the coupon coated with Elastuff™ 101. Leachate from one of the Elastuff™ 101 coupons contained one PBDE congener. PBDE-

209 was detected at a concentration of 0.010 ug/L. It was not detected in the other two replicates. The laboratory qualified the result as estimated because the initial calibration was recovered high. This single data point does not allow determination of whether this detection is real or an artifact of laboratory procedures.

No other coupons released either phthalates or PBDEs to the leachate above the method blank contaminant threshold. Appendix D includes data tables for all the SPLP organics.

Table 21. Detected PAHs in SPLP leachate.

Coupon Code	1-Methyl naphthalene	2-Methyl naphthalene	Anthracene	Fluorene	Naphthalene	Phenanthrene	Pyrene
SNO-01	✓	✓					
SNO-03	✓	✓					
ASW-01				✓			
ASW-02		✓					
ASW-03	✓	✓					
ESW-03		✓					
SIL-01	✓	✓					
SIL-02	✓	✓					
ALA-01	✓	✓				✓	
ALA-02	✓	✓				✓	
ALA-03	✓	✓		✓	✓	✓	✓
EPB-01			✓			✓	
EPB-02	✓	✓					
EPB-03	✓	✓					
SYN-03						✓	

Coating identification codes are defined in Tables 19 and 20 on previous pages.

HDPE Leaching Analysis

The gutters used in this study for collection of runoff were constructed of HDPE and lined with Teflon®. Staff were concerned that the thin Teflon® liner could eventually become damaged, exposing the runoff to phthalates that may be contained in the HDPE.

Results of the 24-hour HDPE DI water leaching analysis indicated detectable concentration of bis (2-ethyl hexyl) phthalate (DEHP), but at less than five times the method blank contamination. Thus, one cannot conclusively say whether or not the DEHP leached from the HDPE. Further, this analysis represents only a single leaching test, with short duration of exposure, conducted at a neutral pH, rather than the slightly acidic pH of rain in western Washington. Finally, the test was conducted only on new HDPE materials rather than on aged materials. Because the analysis was not conclusive, the results of this test should not be extrapolated to other studies.

Discussion

Pilot-Scale Roofing Assessment

Rain Event Information

During the study period (January 29 and April 19, 2013), 313 mm of cumulative precipitation fell on the panels; of this amount, the study captured and sampled a total of 106 mm, representing 34% of the amount that fell. The sampled rain events represented between the 52nd and 91st percentile of the rainfall in a 24-hour period for this location; and average intensities ranged between the 40th and 96th percentile (Howie and Labib, pers. comm., 2012). Sampling lower precipitation volumes would be possible only if a smaller suite of analytes were to be analyzed (e.g., sampling only for metals). Following the protocols used, the minimum rainfall necessary to meet the analytical volume needs was 2.54 mm.

The range of antecedent dry conditions, presented in Table 9 (page 56), represents the full range of conditions defined by the QA Project Plan (Ecology, 2013a) within the six hours preceding a sampling event. Precipitation during the antecedent dry periods ranged from 0 to nearly 2.5 mm. The number of hours with no measurable rain preceding a sampling event ranged from 0 to 66.5, with the greatest numbers of dry hours preceding Events 9 and 10. Events 9 and 10 were not consistently associated with higher concentrations of analytes. A tighter definition of the antecedent dry conditions may reduce stormwater runoff variability and should be considered in any future study.

Volumes Recovered

Ecology measured the depth of runoff recovered in each stainless-steel container for each rain event and calculated volumes. For each event and panel, the volumes recovered were divided by the volume that theoretically fell on the panel-specific square footage (based on precipitation from the onsite gage). The values were then converted into percentages. Table 22 lists the calculated median percents of runoff recovered from each panel across rain events. For these calculations, staff omitted Event 5 because the volumes recovered from all panels during Event 5 were extraordinarily high. Ecology hypothesized that staff may have systematically measured the depth of runoff in the containers incorrectly that day. The calculation does not include a very low recovered volume from the concrete tile (CTI) panel during Event 4, as the low volume resulted from improper alignment between the gutter and the collection container.

Table 22 highlights three noteworthy observations.

- Ecology recovered more than 100% of the theoretical runoff for all of the steep-slope panels. This may have been an artifact of the low resolution of the depth measuring device for the receiving containers. The measuring device was marked in 1-centimeter increments, which represented approximately one liter of volume in the containers. As a result, volume measurements were accurate only to the nearest half liter. However, this error represented a less than 4% recovery for the rain event with the lowest precipitation.

- The three built-up roofing types (BUR, BUA, and BUS) consistently recovered less than 100% of the precipitation volume. This may be attributed to at least two factors. First, the cap sheet materials provided a higher coefficient of friction than other low-slope panels, potentially retarding flow to the gutter. Second, the built-up roofing materials had a greater curvature along the long axis of the panels compared to the single-ply roofing materials. This may have resulted in lower exposed surface areas on the built-up roofing panels.
- The single-ply, low-slope panels (PVC, EPD, and TPO) retained condensate and moisture from non-sampled events, until they reached a threshold and then released water to the gutters. All three of these panels recovered approximately 100% of the rain events.

Table 22. Median percent recoveries of panel runoff across all rain events.

Roof Description	**Roof ID Code**	**Median % Rain Recovered**
Steep-Slope Panels		
Asphalt shingle with AR	AAR	104
Asphalt shingle 1	AS-1	106
Asphalt shingle 2	AS-2	104
Asphalt shingle 3	AS-3	104
Copper	CPR	104
Concrete tile	CTI	104
Painted metal	PAZ	105
Cedar shake treated w/ CCA	TWO	104
Cedar shingle	WOS	102
Glass control, steep slope	GST	106
Low-Slope Panels		
Built-up w/APP	BUA	90
Built-up	BUR	88
Built-up w/SBS	BUS	79
EPDM	EPD	99
Polyvinyl chloride	PVC	103
Thermoplastic polyolefin	TPO	99
Zincalume®	ZIN	100
Glass control, low slope	GLO	103

Total Metals

Analyses of Total Metals in Runoff

Ecology evaluated the concentrations of total metals that leached from the new roofing materials using box and whiskers plots across the 10 rain events, Figures 9-12. Ecology created box plots using R version 2.15.2 (R Core Team, 2012). The box plots, particularly when plotted on the log scale, enable one to quickly identify differences between roofing materials for each of the metals. The panel types (as defined in Table 2, page 40) are identified along the x axis and throughout the report. AS^A represents the average of the three replicate asphalt shingle panels.

The thicker center line of each box represents the 50th percentile (i.e., the median); the upper and lower ends of each box represent the 75th and 25th percentiles of the distribution of the concentrations, respectively. The upper whiskers represent the highest measured value; the lower whiskers represent either the lowest measured value or a value of one-half the MDL, if the metal was not detected.

The asterisks above the box plots indicate that statistically significant differences were found between the panel identified and the appropriate glass control panel (GST for steep-slope panel or GLO for low-slope panel). Ecology used the non-parametric Wilcoxon signed-rank test for statistical comparisons. Non-parametric statistical analyses are routinely used when data violate the assumptions of parametric statistics. Non-parametric analyses are appropriate for environmental data such as stormwater data which are not normally distributed. The Wilcoxon signed-rank test compares data which are paired (e.g., comparing the concentrations of a metal taken from two types of roofing materials over an equal number of rain events). All statistically significant differences identified in Figures 9-12 are one-tailed comparisons measured at $\alpha = 0.005$.

The total cadmium data were not plotted because the majority of the runoff samples had concentrations below the MDL. Each of the metals is discussed below.

Arsenic

Except for the treated wood shake (TWO) and the PVC panels, arsenic concentrations released in the runoff were low. The box and whiskers plot (Figure 9) shows a wider range of variability for those panels that had lower median concentrations. This is a function of the low precision and accuracy near the MDL. The runoff from the glass control panels (GST and GLO) contained low levels of arsenic. The highest arsenic concentrations in runoff from the steep-slope and low-slope controls were 0.70 and 0.34 ug/L, respectively. The median values for all panels, except the treated wood shake (TWO) and PVC panels, were less than these values.

The treated wood shake panel (TWO) was treated with chromated copper arsenate (CCA). Although the shakes did not meet the paperwork requirements of the Western Wood Preservers Institute (WWPI) best management practices (BMPs) to minimize leaching (Brooks, email comm., 2013), the shakes did meet the substantive BMPs designed to reduce leaching (Gruber, pers. comm., 2013). The treated wood shake panel consistently released the highest concentrations of arsenic. Total arsenic from this panel had a median concentration of 1,610 ug/L and ranged in concentration from 692 to 4,690 ug/L, which was significantly higher than the steep-slope glass control panel (GST).

The PVC panel released the second highest concentrations of arsenic (median value of 38 ug/L), almost two orders of magnitude lower than runoff from the treated wood shake panel (TWO) Total arsenic from the PVC panel ranged between 22 and 117 ug/L. The PVC panel was also significantly higher than the steep-slope glass control panel (GST). Arsenic was thought to be attributable to its use as a biocide in the PVC formulation (RTF, pers. comm., 2013).

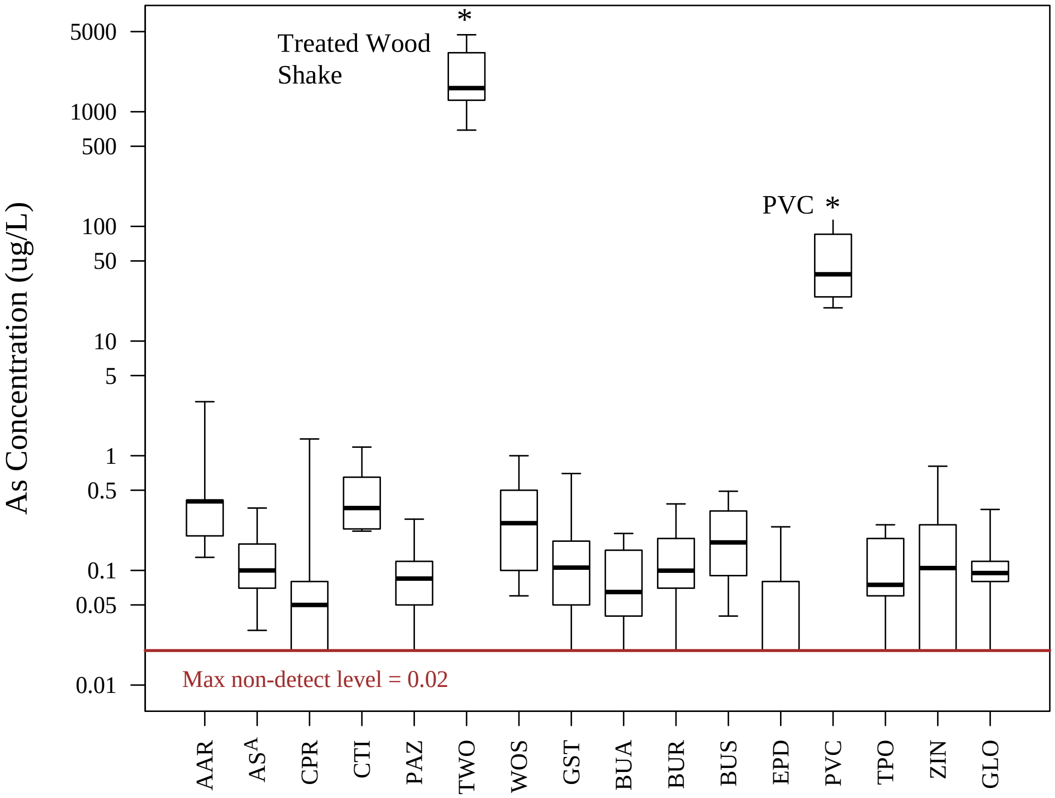

Figure 9. Box plots for total arsenic concentrations across all panels.

Panel identification codes are defined in Table 2 on page 40.

Cadmium

Total cadmium concentrations in runoff from most panels were very low. Cadmium concentrations in the runoff ranged from non-detected values (MDL of 0.01 ug/L) for the majority of both steep- and low-slope panels to detections just above the MDL (Figure 5, page 62).

The treated wood shake panel (TWO) consistently had the highest measurable concentrations of cadmium, ranging between 0.07 and 0.26 ug/L. Using the Wilcoxon signed-rank test, runoff from the treated wood shake panel (TWO) was significantly higher than the steep-slope glass control panel (GST). Runoff from the copper panel was also significantly higher than the steep-slope glass control panel (GST).

The other new roofing materials released concentrations similar to those released from the glass control panels. The number of non-zero differences did not allow statistical comparisons. The majority of the roofing materials tested do not appear to be substantial contributors of cadmium, especially when the concentrations of the glass control panels, from aerial deposition, are considered.

Copper

The box and whiskers plot (Figure 10) shows that the copper panel (CPR) and the treated wood shake panel (TWO) had the highest measured concentrations of copper in the runoff. Most of the other panels were two to three orders of magnitude below the concentrations on these two panels. Runoff from the treated wood shake panel (TWO) ranged five-fold from 601 to 3,190 ug/L, depending on rain event, while the copper panel released more consistent concentrations in the runoff, ranging from 1,035 to 3,380 ug/L. Both the treated wood shake (TWO) and copper (CPR) panels were significantly higher than the steep-slope glass control panel (GST).

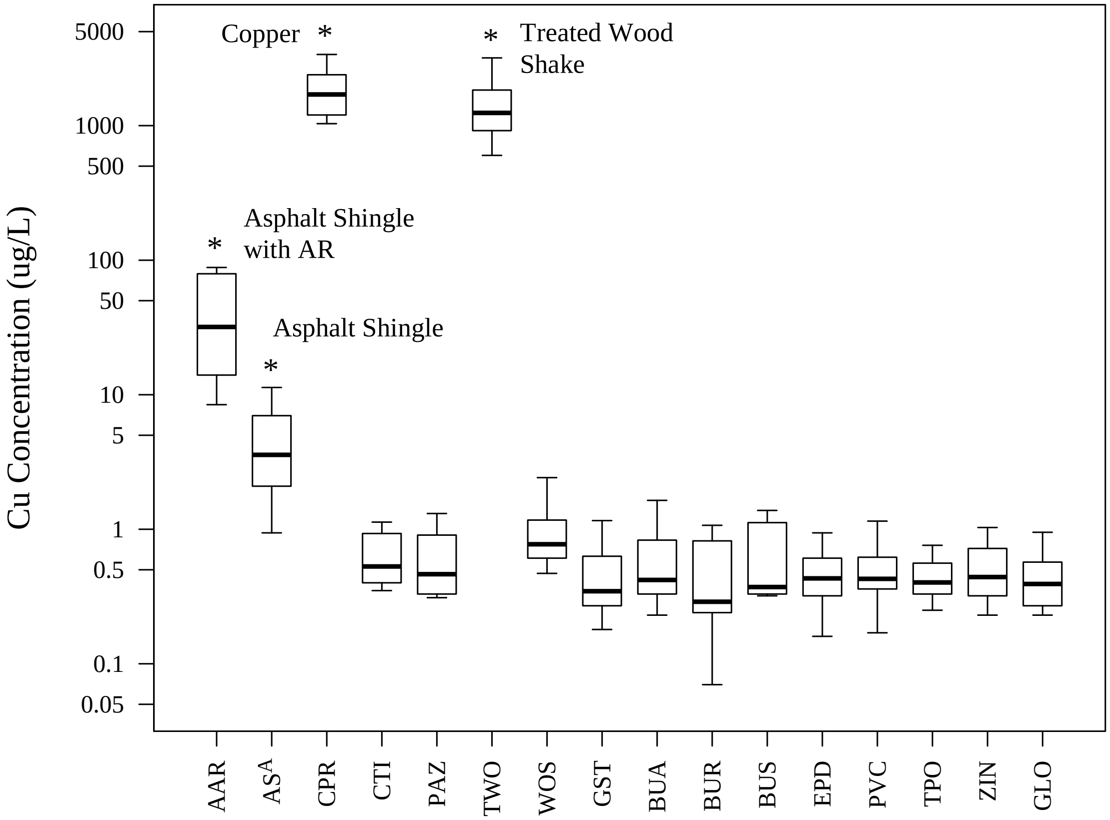

Figure 10. Box plots for total copper concentrations across all panels.

Panel identification codes are defined in Table 2 on page 40.

Concentrations in runoff from the asphalt shingle panel with AR (AAR) ranged between 12 and 88 ug/L (with a median concentration of 32 ug/L). The three replicates of the asphalt shingle panel without AR (AS^A) had a median concentration of copper in the runoff of 3.6 ug/L. Concentrations of copper in runoff from the asphalt shingle panel with AR (AAR) were higher than from the asphalt shingle panels without AR. This would be expected as AR treatment includes time-release copper granules designed to release copper to reduce algal growth. The copper levels in runoff from both of these roofing materials were also significantly higher than from the steep glass control panel (GST).

The three replicates of the asphalt shingle panel without AR (AS^A) were evaluated to determine whether there were differences in copper concentrations released in the runoff from each of the panels. In a pair-wise comparison of runoff from each of the three panels using the Wilcoxon signed-rank test, runoff from AS-3 had significantly higher copper concentrations than runoff from AS-2 (a one-tailed test at $\alpha = 0.05$), but not than from AS-1. AS-1 and AS-2 were also not significantly different from one another.

Because each of the three asphalt shingle panels included a random placement of the shingles from the six asphalt shingle manufacturers in the Pacific Northwest, these differences warranted further investigation. At the suggestion of the Roofing Task Force, Ecology analyzed the shingles on the three panels more thoroughly using XRF analysis to assess whether the copper concentrations in the shingles could be different. Staff conducted three XRF analyses of each of the six types of shingle on each of the panels. One type of shingle was found to have higher copper concentrations (ranging from 166 to 630 ppm) than the other shingles (ranging from the limit of detection to 68 ppm). The range of these higher copper XRF readings was within the range measured on the non-AR coupons (within the sensitivity of the XRF) as previously discussed and represented in Table 7 (page 53).

Differences were assessed for the one shingle type across the three replicate asphalt shingle panels. XRF analyses revealed that Panel AS-3 had the highest average copper concentrations (464 ppm) compared with AS-1(397 ppm) and AS-2 (371 ppm). Three rows of this type of shingle were installed on each of the three asphalt shingle panels. All of these shingles came from a single lot. The shingle manufacturer indicated that the variation between panels may be manufacturing variation, even within lot variation. The higher concentration of copper on the one type of asphalt shingle on AS-3, likely contributed to the statistically higher copper concentrations released in the runoff from AS-3 than from AS-2.

Lead

Lead concentrations, while measurable, were low and variable across all roofing materials, as evidenced from Figure 11. Median lead concentrations in the runoff ranged from a low of 0.05 ug/L from the asphalt shingle with AR panel (AAR) to 0.28 ug/L from the concrete tile panel (CTI). Lead concentrations in runoff from the glass control panels (GST and GLO) were greater than runoff from a number of roofing types and within the range of all releases from new roofing materials. The new roofing materials do not appear to be substantial contributors of lead to the runoff.

Lead in runoff from the steep-slope glass control panel (GST) was found to be significantly higher than from the treated wood shake panel (TWO). This implies that either the glass was a source of lead or that lead in the atmospheric deposition was absorbed by the porous wood. Ecology does not have sufficient information to differentiate between these two possible reasons for the difference.

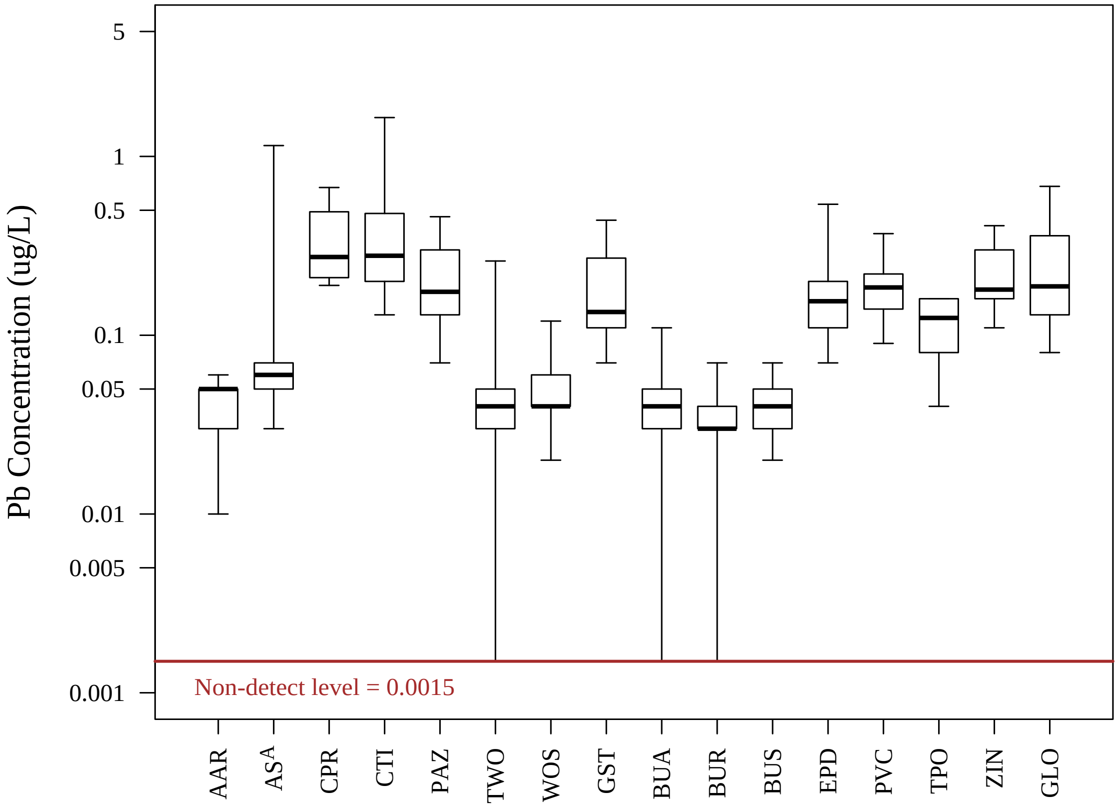

Figure 11. Box plots for total lead concentrations across all panels.

panel identification codes are defined in Table 2 on page 40.

Zinc

All panels released measureable concentrations of zinc in the runoff (Figure 12). Runoff from the Zincalume® panel (ZIN) had the highest concentrations of total zinc, which ranged from 38 to 578 ug/L. Zinc concentrations released from the Zincalume® panel were significantly higher than zinc concentration in runoff from the glass control panel (GST).

The new EPDM roofing material (EPD) also released significantly higher concentrations of zinc than the low-slope glass control panel (GLO). EPDM runoff concentrations ranged from 44 to 313 ug/L. EPDM is a product that uses zinc as a catalyst in the manufacturing process, similar to tires (Fisler, pers. comm., 2013); therefore, and the zinc catalyst may be the source of zinc in the runoff.

The painted galvanized steel panel (PAZ) released between 18 and 83 ug/L of zinc. Runoff from the painted galvanized steel panel (PAZ) was significantly higher than the zinc concentration in runoff from the steep-slope glass control panel (GST). Zinc may have leached from the unpainted, galvanized edge of the roof material.

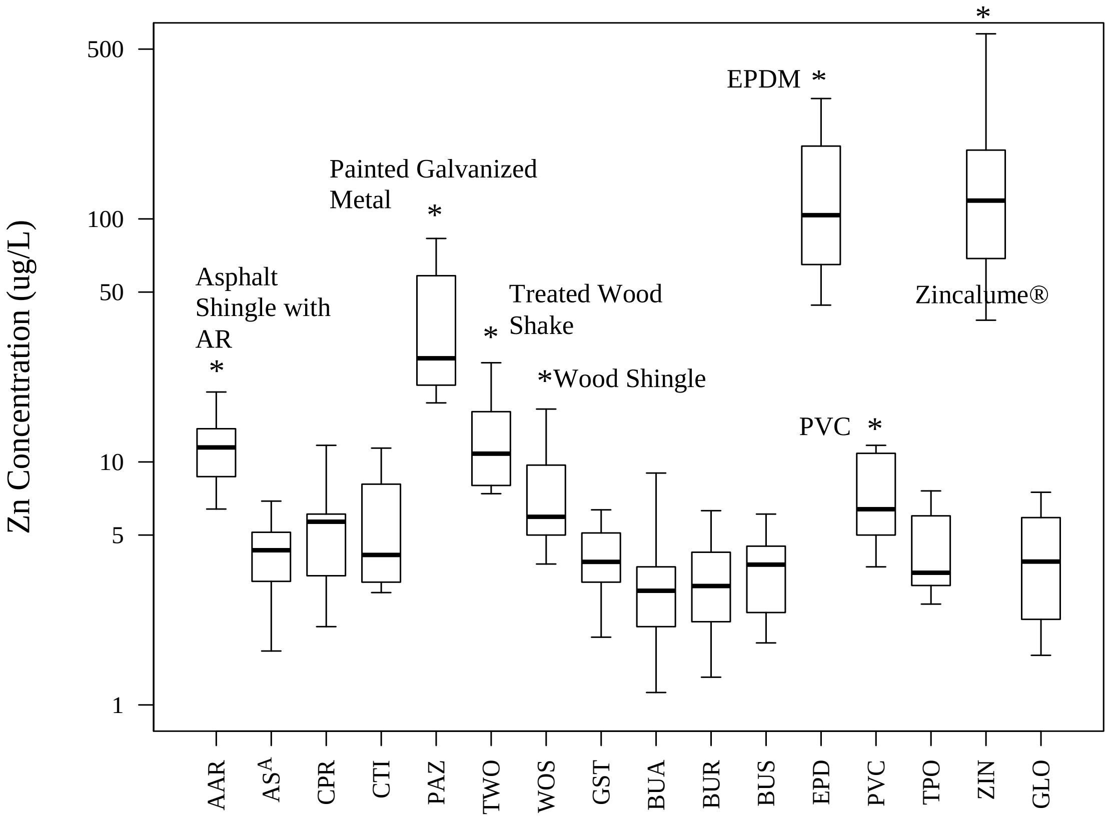

Figure 12. Box plots for total zinc concentrations across all panels.

Panel identification codes are defined in Table 2 on page 40.

Zinc concentrations in the runoff from the following panels were 10 to 100 times lower in zinc concentrations than runoff from the Zincalume® and EPDM panels, but the runoff from each panel was significantly higher than their respective glass control panels:

- Treated wood shake roof (TWO)
- Wood shingle roof (WOS)
- Asphalt shingle with AR roof (AAR)
- PVC roof

Total Metals Released

Ecology calculated the total metals released (sometimes termed *mass load*) for each of the roofing materials assessed as specified in the QA Project Plan (Ecology, 2013a). Ecology calculated these by multiplying the concentrations by the volume recovered from each rain event, and dividing by the projected surface area, then subtracting the glass control panels and calculating the medians. The medians do not include Event 5, for which the recorded volumes were suspect. Table 23 lists the median release rates for the 10 rain events and roofing materials sampled in this project.

Table 23. Median total metals released (in ug/m^2) minus glass control panels.

Metal	Steep-Slope Panels						
	AAR	**AS[A]**	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**
Arsenic	1.4	0.18	-0.2	2.8	0.09	17,621	0.68
Cadmium	0.01	0.02	0.09	0.01	0.01	1.3	0.00
Copper	325	47	18,855	1.7	1.1	11,966	4.0
Lead	-1.0	-0.87	1.3	1.2	0.38	-0.9	-0.90
Zinc	57	-8	16	14	305	64	9
Metal	**Low-Slope Panels**						
	BUA	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**
Arsenic	-0.32	0.02	0.36	-0.46	355	-0.09	0.04
Cadmium	-0.01	-0.01	-0.01	0.00	0.01	0.00	0.02
Copper	2.1	-0.65	0.07	0.16	0.24	0.28	0.15
Lead	-1.6	-1.7	-1.8	-0.65	-0.12	-0.87	-0.41
Zinc	-10	-11	-16	918	37	11	797

[A] Average of three replicate asphalt shingle panels.
Panel identification codes are defined in Table 2 on page 40.

These release rates should not necessarily be applied directly to other studies for at least three reasons:

- The lowest volume rain event collected in this study represents the 52%ile of the 24-hour rainfalls in this location. Thus, lower precipitation events are not represented.
- As described in the next section, the relationship between precipitation and concentration is not linear. As precipitation increases, the concentrations of metals decrease. Thus, one would expect that the lower misty rainfalls typical of the Puget Sound basin may release more metals than listed in Table 23.
- The panels used in this study represented less than 3 meters of run length, much less than on normal residential or commercial roofs. Bielmyer et al. (2011) found that contact time increased the concentrations in runoff. Thus longer run length roofs would likely release greater metals loads than the values in Table 23.

Impacts of Precipitation Amount

For those roofing panels with more elevated concentrations of total metals, Ecology evaluated the relationship between the depth of rain and the concentration. Figures 13 through 15 plot concentration of total metals versus precipitation depth for arsenic, copper, and zinc, respectively, for those panels releasing high concentrations of metals. The simple regression performed in Excel resulted in inverse log-normal relationships with r^2 values ranging from 0.53 to 0.85. The greater the rain depth, the lower the concentration of the metal.

He et al. (2001) and Jungnickel et al. (2008) reported similar relationships. In assessing the relationship between precipitation intensity and loading, He et al. found that at low intensity (drizzle of 1 mm/hr) copper load increased. In the case of He's study and the Jungnickel et al. (2008) study for the higher concentration metals (arsenic, copper, and zinc), the relationships between concentration and rain volume were pronounced. These relationships may be a function of the first-flush effect delivering higher concentrations of contaminants, which is well documented (Bannerman et al., 1993; Steuer et al., 1997; and Boller et al., 1997).

Based on the inverse relationships identified between concentration and rainfall depth, Ecology's intention as specified in the QA Project Plan (Ecology, 2013a) of calculating the median concentration per mm of rain could mislead readers into thinking that a linear and increasing relationship could be projected. Thus, Ecology did not calculate concentration per millimeter of rain.

Ecology assessed potential correlations between the following sets of factors but found no correlations:

- Average rain event intensity (volume divided by duration) and concentration
- Average rain event intensity when rain was falling (volume divided by duration only when precipitation was recorded) and concentration
- pH and concentration
- Length of antecedent dry period and concentration
- Wind speed and concentration
- Wind direction and concentration
- Rain event duration and concentration
- Rain event date and concentration
- Rain intensity and mass released (load)

With additional data, some of these relationships may become apparent.

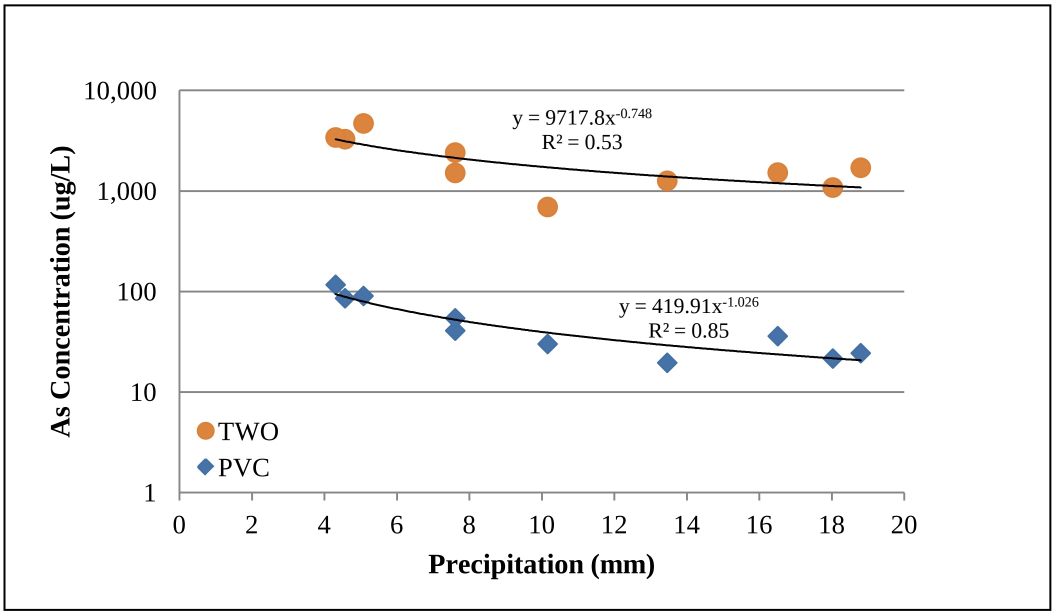

Figure 13. Arsenic concentration versus rain depth for treated wood and PVC panels.

Panel identification codes are defined in Table 2 on page 40.

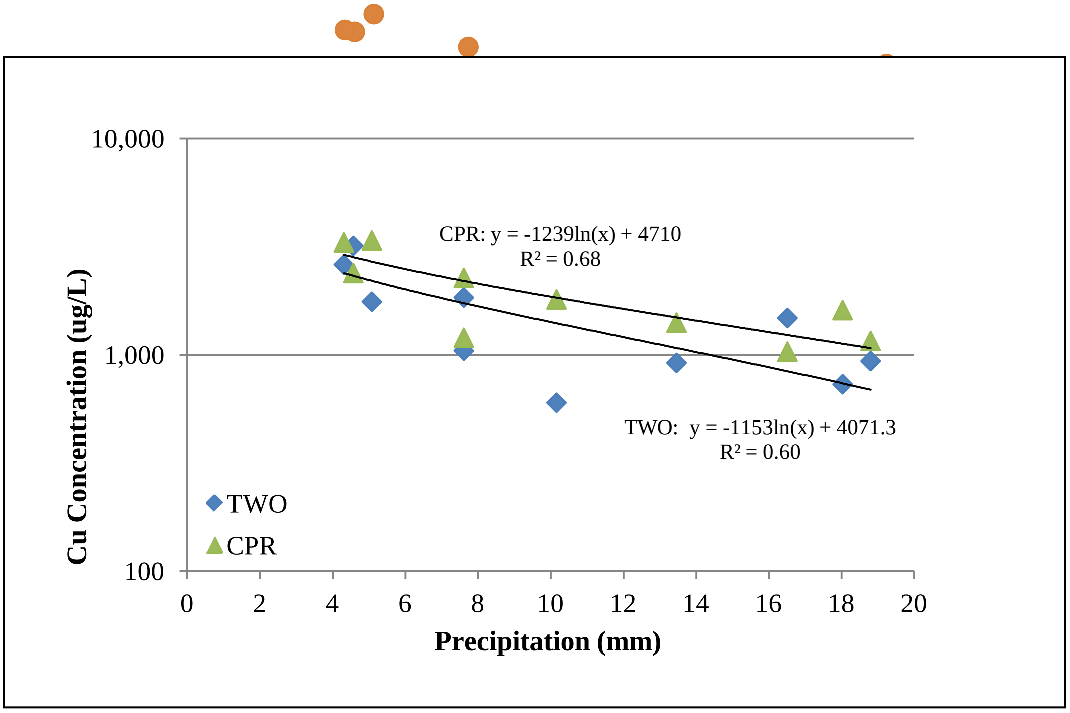

Figure 14. Copper concentration versus rain depth for treated wood and copper panels.

Panel identification codes are defined in Table 2 on page 40.

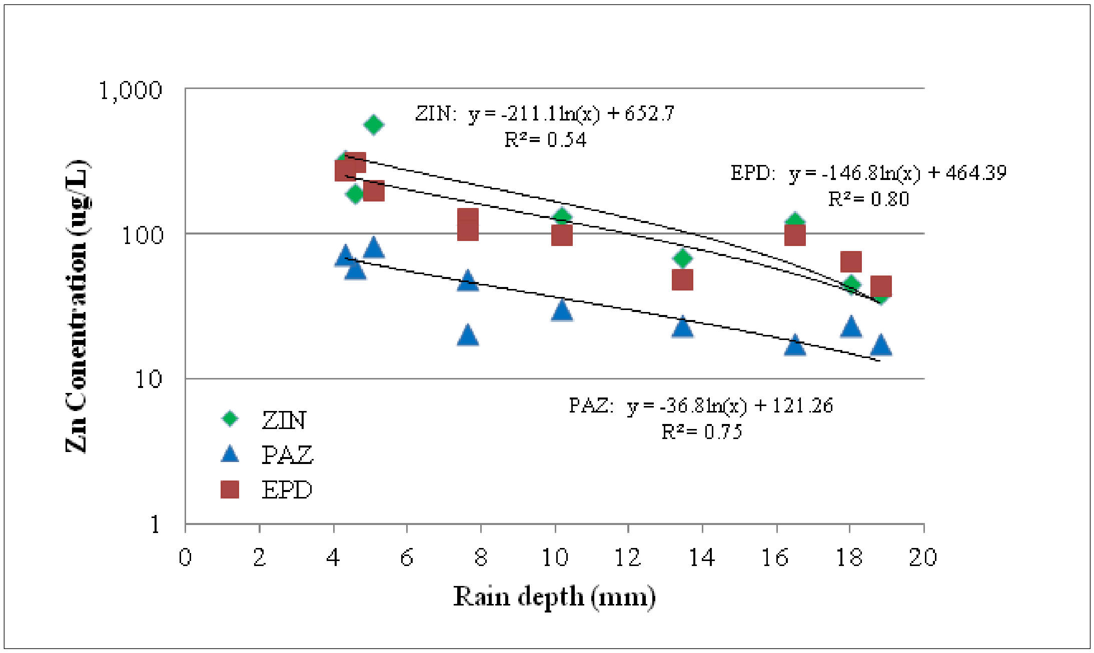

Figure 15. Zinc concentrations versus rain depth on Zincalume®, EPDM, and painted galvanized steel panels.

Panel identification codes are defined in Table 2 on page 40.

Total Metals Comparisons with Other Studies

Comparison with the Puget Sound Toxics Assessment

Concentrations of metals in runoff obtained in this study were compared to release estimates within the Puget Sound basin from the Puget Sound Toxics Assessment (Ecology, 2011a). These comparisons are shown in Table 24 for similar roofs.

For copper in runoff from the copper (CPR) panel, and arsenic in runoff from the asphalt shingle panel with AR (AAR), values were similar (indicated by yellow shading in the table). With these two exceptions, this comparison reveals that concentrations used in the Puget Sound Toxics Assessment (Ecology, 2011a) ranged from double to two orders of magnitude higher. For example, zinc concentrations in runoff from the Zincalume® panel (ZIN) are an order of magnitude lower than mean concentrations used in the Puget Sound Toxics Assessment. However, runoff concentrations used to estimate releases to the Puget Sound basin (Ecology, 2011a) were based predominantly on roofing systems (full-scale roofs with components), rather than roofing materials alone.

Table 24. Comparisons of concentrations of metals (in ug/L) used to estimate releases in Puget Sound to those in this study.

Metal	Arsenic	Cadmium	Copper	Lead	Zinc
Ecology 2011a Estimates (mean of literature values used)					
Asphalt shingle	*0.3*	0.7	10	25	1,340
Metal	-	0.8	355[a]	5	2,860
Copper	-	-	*1,690*	-	-
Concrete tile	-	-	-	-	94
Wood	-	-	-	0.8	7,390
Built-up	-	1.4	23	27	221
Current Roofing Assessment (medians)					
AAR	*0.4*	<0.1	32	<0.1	11
AS[A]	0.1	<0.1	3.6	<0.1	4.4
Metal (PAZ and ZIN)	0.1	<0.1	0.4 - 0.5	0.2	27 - 119
Copper	0.1	<0.1	*1,708*	0.3	5.7
CTI	0.4	<0.1	0.5	0.3	4.2
Wood (treated)	1,610	0.14	1,263	<0.1	11
BUR	0.1	<0.1	0.3	<0.1	3.1
Single-ply panels (EPDM, PVC, TPO)	<0.1 - 38	<0.1	0.4	0.1 - 0.2	4 - 104

[a] This value is based on the average of the value reported by Good (1993) and a value misread from a chart reported by Tobiason (2004).

[A] Average of three replicate asphalt shingle panels

Panel identification codes are defined in Table 2 on page 40.

Yellow-highlighted, italicized cells indicate similarities with this study.

Low metals concentrations released from the new roofing materials assessed in this study would seem to imply one or more of the following:

- Components of roofing systems, other than the roofing materials evaluated, could contribute to the higher concentrations reported for roofing systems;
- Existing galvanized metal roofs in the Puget Sound region contribute higher concentrations (and mass) than concentrations measured from the Zincalume® panel in this study; or
- The length of the pilot panels assessed in this study does not simulate actual roofing lengths. Bielmyer et al. (2011) suggest that residence time (contact time) of a drop of precipitation on a roofing surface is positively correlated to the length of a roofing panel. Note that several of the authors whose values were used to estimate releases in the Ecology (2011a) study employed pilot-scale roofing panels without the full complement of roofing components.)

Comparison with Other Literature

Ecology calculated the median concentrations released for each panel. Because some of the metals could have originated from sources other than the roofing materials, (e.g., from aerial deposition), Ecology also calculated a median concentration for each metal by roofing material across all rain events and subtracted the median glass control panel concentration (using either the steep-slope or low-slope glass panels, as appropriate). Table 25 shows the results.

Subtraction of concentrations measured from the control panels is the same technique used by Clark (2010) and Chang et al. (2004). As shown in Table 25, these calculations resulted in negative values for some metals concentrations indicating that the roofing materials associated with the negative values were not a likely source for that metal.

Table 25. Median total metals concentrations (in ug/L) by panel minus the median concentrations on glass control panels.

Metal	**Steep-Slope Panels**							
	AAR	**AS[A]**	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**	**GST**
Arsenic	0.28	-0.02	-0.07	0.23	-0.04	1,610	0.14	NA
Cadmium	0.00	0.002	0.015	0.00	0.003	0.130	0.00	NA
Copper	31.6	3.29	1,707	0.18	0.13	1,262	0.43	NA
Lead	-0.09	-0.07	0.14	0.15	0.04	-0.10	-0.10	NA
Zinc	7.58	0.48	1.78	0.25	23	6.93	2.05	NA
Metal	**Low-Slope Panels**							
	BUA	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
Arsenic	-0.03	0.01	0.09	-0.08	38	-0.02	0.02	NA
Cadmium	0.00	0.00	0.003	0.00	0.00	0.00	0.003	NA
Copper	0.03	-0.10	-0.02	0.05	0.04	0.01	0.05	NA
Lead	-0.16	-0.15	-0.15	-0.04	-0.01	-0.07	-0.01	NA
Zinc	-0.95	-0.80	-0.10	100	2.65	-0.40	115	NA

[A] Average of three replicate asphalt shingle panels.
NA: Glass control panel values have been subtracted.
Shading indicates control panels.
Panel identification codes are defined in Table 2 on page 40.

The median metals concentrations in Table 25 were compared to other studies in the literature cited in Table 1 (page 25) and discussed by type of roofing materials below. Studies by Clark (2010) and Chang et al. (2004) are particularly comparable because these researchers used designs similar to those of this study. They used pilot-scale roofing panels rather than whole roofing systems, collected whole rain events, and subtracted “aerial deposition” measured on their control panels. Note that the Chang et al. (2004) study collected runoff samples using galvanized gutters, increasing the concentrations of zinc in the samples collected. Their study was also conducted downwind of a zinc emitting industry (TDC, 2013). These two factors likely led to the higher concentrations of zinc recorded in that study.

For each of the categories of roofing materials in Tables 26 through 33, green-highlighted results represent the current study. Yellow-highlighted concentrations from the literature represent concentrations similar to those found in this study. Similarities were identified where the concentrations in this study were very low and the literature result was undetected, and where concentrations were within 70% of one another. In each of these tables, the notes identify whether authors studied full-scale roof systems or panels.

Asphalt Shingle Roofs

Table 26 compares metals in the runoff from asphalt shingle roofing materials.

- The Clark (2010) study evaluated shingles with AR. Her reported total metals concentrations were more similar to the low concentrations for arsenic, cadmium, and lead in the runoff from the new asphalt shingle roofing panels (AS^A) in this study. The asphalt shingles with AR (AAR) in this study showed higher concentrations of copper than the Clark study.
- The metals concentrations in runoff from the asphalt shingle panels with AR (AAR) were similar to the metals concentrations reported by Mendez et al. (2010), although the zinc concentrations in the Mendez study were higher.
- Copper concentrations in the runoff from asphalt shingle panels with AR (AAR) in this study were similar to the runoff from the panel in the Chang et al. (2004) study. Zinc and lead concentrations in runoff in the present study were lower than those in the Chang et al. (2004) study. The elevated zinc concentrations in the Chang et al. (2004) study are likely attributable to the galvanized gutters.
- Zinc concentrations in runoff from asphalt shingle roofing systems studied by Steuer et al. (1997) were higher than this study. Their higher concentrations were likely due to monitoring complete roofing systems with flow through gutters and downspouts and their full-length roofs.

Table 26. Comparisons of concentrations of metals (in ug/L) in runoff from asphalt shingle panels and roofs in the literature with those in this study.

Roof Type	**Location**	**As**	**Cd**	**Cu**	**Pb**	**Zn**	**Notes**	**Author**
AS^A	WA	-0.02	0.002	3.29	-0.07	0.48	P	Ecology (2014)
AAR	WA	0.28	0.0	32	-0.09	7.6	P	Ecology (2014)
Asphalt shingles with AR	PA	0.3	*ND*	ND	*ND*	*ND*	P	Clark (2010)
Asphalt shingle - galv gutter	TX			*25*	38	554	P, g	Chang et al. (2004)
Asphalt fiberglass shingles	TX	*<0.29*	*<0.10*	*26*	0.6	28	P	Mendez et al. (2010)
Asphalt - residential	MI & WI			0.7	10	318	RS	Steuer et al. (1997)

^{A} Average of three replicate asphalt shingle roofs
g: Galvanized gutters
ND: Not detected
P: Panel
RS: Installed roofing system
Yellow-highlighted, italicized cells indicate similarities with this study.

Copper Roofs

The copper roof panel (CPR) produced runoff concentrations similar to those reported by Pennington and Webster-Brown (2008) for eight-year-old roofs (Table 27). The lack of similarity with the aged copper roofs reported in Connecticut by Boulanger and Nikolaidis (2003), and those reported by Persson and Kucera (2001) in Sweden, may be attributed to more acidic rain in the study areas and their assessments of full-scale roof systems.

Table 27. Comparisons of concentrations of metals (in ug/L) in runoff from copper roofs in the literature with this study.

Roof Type	**Location**	**As**	**Cd**	**Cu**	**Pb**	**Zn**	**Notes**	**Author**
CPR	WA	-0.07	0.015	1,707	0.14	1.8	P	
Copper	Sweden			3,575			P	Persson & Kucera (2001)
Copper 8 years old	New Zealand			*1,976*			RS	Pennington & Webster-Brown (2008)
Copper 11 years old	CT			2,660		31	RS	Boulanger & Nikolaidis (2003)

P: Panel
RS: Installed roofing system
Yellow-highlighted, italicized cell indicates similarities with this study.

Concrete Tile Roofs

The concrete tile panel (CTI) in this study showed few similarities with concentrations of metals in runoff from tile roofs in the literature (Table 28), except for cadmium in the panel studied by Mendez et al. (2010). Differences may be attributable to differences in concrete source materials.

Table 28. Comparisons of concentrations of metals (in ug/L) in runoff from concrete tile roofs in the literature with those in this study.

Roof Type	**Location**	**As**	**Cd**	**Cu**	**Pb**	**Zn**	**Notes**	**Author**
CTI	WA	0.23	0.0	0.18	0.145	0.25	P	Ecology (2014)
Concrete tile	TX	0.42	*<0.10*	5.3	1.3	91	P	Mendez et al. (2010)
Concrete tile	Malaysia				197	94	RS	Yaziz et al. (1989)
Concrete tile	Sweden			<20	3.5	25	P	Persson & Kucera (2001)

P: Panel
RS: Installed roofing system
Yellow-highlighted, italicized cell indicates similarities with this study.

Pre-painted Galvanized Roofs

The literature generally reported higher concentrations of zinc in runoff from pre-painted metal roofs than in this study (Table 29). Zinc concentrations reported in the Robert-Saint et al. (2009) study were most similar, possibly because the roof was painted with a polyester coating similar to the paint in this study. Differences in the other studies cited in Table 29 compared to this study may be a function of the age of the materials, chemical formulations of the paint, and/or assessment of whole roofing systems compared to roof panels.

Although Taylor (2004) investigated post-manufactured painting, his results merit noting. He reported up to 87% reductions in the zinc concentrations released using a synthetic rain application. Tobiason et al. (2006) found general reductions of approximately 37% in the total zinc released from a Galvalume® surface after painting and subsequent removal of gutter sediments.

Table 29. Comparisons of concentrations of metals (in ug/L) in runoff from pre-painted galvanized steel roofs in the literature with this study.

Roof Type	**Location**	**As**	**Cd**	**Cu**	**Pb**	**Zn**	**Notes**	**Author**
PAZ	WA	-0.04	0.003	0.13	0.04	23	P	Ecology (2014)
Prepainted Zincalume®	WA			1.3		146	RS	Herrera (2011)
Prepainted galvanized steel	Sweden					160	P	Heijerick et al. (2002)
Painted steel	Sweden					2,100	P	Persson & Kucera (2001)
Prepainted galv steel. Stainless with Zn coating and polyester top coat	France		ND	2.9	0.5	*31*	P	Robert-Saint et al. (2009)

PAZ: Manufacturer-painted galvanized steel, painted with silicone-modified polyester paint
P: Panel
RS: Installed roofing system
ND: Not detected
Yellow-highlighted, italicized cell indicates similarities with this study.

Treated and Untreated Wood Roofs

Table 30 provides concentrations of metals in runoff from untreated and treated wood panels and led to the following statements:

- Untreated wood shingles (WOS) released few metals. Comparison with Khan et al. (2006) (not in Table 30) and Clark (2010) showed similar results.
- The treated wood panels that Clark (2010) tested resulted in concentrations of copper within the range of those found in this study for the treated wood shake panel (TWO). Clark's reported zinc concentrations were substantially higher, while her arsenic concentrations were substantially lower than those measured in this study. It appears that the treated wood in Clark's study may have been treated with a copper-containing preservative other than CCA because the measured arsenic in her study was low.
- Arsenic concentrations in runoff from the treated wood panel were higher than the average of 600 ug/L cited by Khan et al. (2006) for CCA-treated deck materials (not in Table 30), but within the range they measured (up to 8,400 ug/L).

Table 30. Comparisons of concentrations of metals (in ug/L) in runoff from untreated and treated wood panels in the literature with those in this study.

Roof Type	**Location**	**As**	**Cd**	**Cu**	**Pb**	**Zn**	**Notes**	**Author**
WOS	WA	0.14	0.0	0.43	-0.10	2.1	P	Ecology (2014)
Cedar shakes	PA	*-0.3*	*-0.2*	-30	0.8	201	P	Clark (2010)
Untreated plywood	PA	*-0.3*	*0.1*	-55	1.6	0.0	P	Clark (2010)
Wood shingle - galv gutter	TX	NM	NM	29	45	16,317	P	Chang et al. (2004)
TWO	WA	1610	0.13	1,262	-0.10	6.9	P	Ecology (2014)
Pressure treated/ water sealed wood	PA	4.2	0.03	1,867	0.1	890	P	Clark (2010)
Pressure treated wood	PA	1.3	0.1	*1,691*	-0.4	-10	P	Clark (2010)

NM: Not measured
P: Panel
Yellow-highlighted, italicized cells indicate similarities with this study.

Built-up Roofs

Table 31 provides literature results for runoff from various built-up roofing materials. The three built-up roofing panels (BUA, BUR, and BUS) in this study resulted in low total metals concentrations in the runoff, unlike the elevated concentrations of zinc and lower concentrations of copper and lead measured for whole roof systems by Bannerman et al. (1993) and Steuer et al. (1997). These two studies used complete roofing systems and included gutters which may have been galvanized metal. The Change and Crowley (1993) study used galvanized gutters and reported elevated zinc concentrations. Mendez et al. (2010) found similar concentrations of arsenic and cadmium in the runoff from their panels, even though aerial deposition was not subtracted for their study.

Table 31. Comparisons of concentrations of metals (in ug/L) in runoff from built-up panels and roofs in the literature with those in this study.

Roof Type	**Location**	**As**	**Cd**	**Cu**	**Pb**	**Zn**	**Notes**	**Author**
BUR	WA	0.005	0.0	-0.10	-0.15	-0.8	P	Ecology (2014)
BUA	WA	-0.04	0.0	0.03	-0.16	-0.95	P	Ecology (2014)
BUS	WA	0.09	0.003	-0.02	-0.15	-0.1	P	Ecology (2014)
BUR with white APP cap sheet	TX	*<0.29*	*<0.10*	1.3	0.6	46	P	Mendez et al. (2010)
Rock and tar (built-up)	TX	NM	NM	NM	12	4,880	RS	Chang & Crowley (1993)
Built-up commercial	WI			9	7	330	RS	Bannerman et al. (1993)
Built-up industrial	WI			6	8	1,155	RS	Bannerman et al. (1993)
Built-up commercial	MI & WI			0.9	23	348	RS	Steuer et al. (1997)

P: Panel
RS: Installed roofing system
NM: Not measured
Yellow-highlighted, italicized cells indicate similarities with this study.

Single-Ply Roofs

Single-ply roofing materials have not been as thoroughly reported in the literature (Table 32). The rubber roofing and Ondura® panels in the Clark (2010) study produced similar concentrations of zinc in the runoff as the EPDM panel in this study. Also similar were the concentrations of cadmium, copper, and lead, from Clark's corrugated PVC control panel and the PVC panels of this study. Especially noteworthy in this study was the elevated arsenic concentration in the PVC runoff, which was thought to be attributable to an added biocide (RTF, pers. comm., 2013).

Table 32. Comparisons of concentrations of metals (in ug/L) from single-ply panels and roofs in the literature with those in this study.

Roof Type	**Location**	**As**	**Cd**	**Cu**	**Pb**	**Zn**	**Notes**	**Author**
EPDM	WA	-0.08	0.0	0.05	-0.04	100	P	Ecology (2014)
Rubber roofing	PA	*-0.3*	1.9	-26	1.3	*94*	P	Clark (2010)
Ondura®	PA	*-0.1*	*-0.1*	-64	0.2	*115*	P	Clark (2010)
PVC	WA	38	0.0	0.04	-0.005	2.7	P	Ecology (2014)
Corrugated PVC	PA	0.1	*-0.3*	*0*	*0.1*	ND	P	Clark (2010)
TPO	WA	-0.02	0.0	0.01	-0.07	-0.4	P	Ecology (2014)
Polyester	Switz.			217	4.9	27	RS, cu	Zobrist et al. (2000)

EPDM: Ethylene propylene diene monomer
cu: Copper gutter
P: Panel
RS: Installed roofing system
ND: Not detected
Yellow-highlighted, italicized cells indicate similarities with this study.

Table 33 provides literatures values for Galvalume® and Zincalume® roofing systems and panels. Zincalume is a trade name for a Galvalume® type product.

- The Zincalume® panel (ZIN) in this study provided results most similar to Mendez et al. (2010) Galvalume® panel despite the fact that the Mendez pilot panels were at steeper slopes.
- The Zincalume® panel (ZIN) resulted in higher zinc concentrations than the 24 ug/L reported by Clark (2010) for a Galvalume® panel, but substantially lower than those reported for a full-scale roof reported by Tobiason (2004).
- The panel results for the Galvalume® and Galfan® reported by Heijerick et al. (2002) may reflect a different manufacturing process, as these were not similar to the values found in this study.
- The Zincalume® panel (ZIN) resulted in zinc concentrations in the runoff approximately one-tenth of those for regular galvanized roofing surfaces reported by Gromaire et al. (2002), Robert-Sainte et al. (2009), Heijerick et al. (2002), Good (1993), and Chang et al. (2004) (Table 1, page 25).

Table 33. Comparisons of concentrations of metals (in ug/L) from Galvalume®, Zincalume, and similar roofs and panels in the literature with those in this study.

Roof Type	**Location**	**As**	**Cd**	**Cu**	**Pb**	**Zn**	**Notes**	**Author**
Zincalume® (ZIN)	WA	0.02	0.003	0.05	-0.01	115	P	Ecology (2014)
Galvalume® (55% aluminum, zinc coated steel)	WA			22		2,890	RS, g	Tobiason (2004)
Galvalume® (55% aluminum, zinc coated steel)	PA	*-0.3*	1.3	-59	2.1	25	P	Clark (2010)
Galvalume®	TX	*<0.29*	*<0.10*	2.2	*0.7*	*118*	P	Mendez et al. (2010)
Galvalume®	Sweden					1,600	P	Heijerick et al. (2002)
Galfan® (aluminum coated)	Sweden					1,600	P	Heijerick et al. (2002)

g: Galvanized gutter
P: Panel
RS: Installed roofing system
Yellow-highlighted, italicized cells indicate similarities with this study.

Dissolved Metals

Ecology measured dissolved metals in runoff from all the roofs during the first three rain events, and not thereafter. Appendix D provides the dissolved metals results.

Table 34 depicts the percentages of dissolved metals represented of the total metals concentrations by roof type. The average values are shown in the table for arsenic, copper, lead, and zinc. For cadmium, most of the total metals concentrations were not detected above the MDL; therefore, the percentages for cadmium would be misleading and are not represented in the table. For arsenic and lead, some of the total metals results were not detected above the MDL, and the percentages were not included in the table as they would also be misleading. In one instance, the dissolved lead value was more than 5 times higher than the total lead value, possibly a contaminant from the filter; this result was not included in the averages in the table.

Those percentages in which the relative standard deviation (RSD) for the three rain events is less than or equal to 15%, and all values were detected for both total and dissolved metals, are highlighted in yellow in the table. These are the percentages considered most reliable.

The following statements can be derived from this limited data set:

- Where metals concentrations were high (e.g., arsenic on TWO and PVC, copper on CPR and TWO, and zinc on ZIN, EPD, and PAZ), the percentages of dissolved metals represent the majority of the metals (between 70 and slightly more 100%).
- For the three built-up roofs (BUR, BUA, and BUS), the percentage of dissolved metals differed from one another.
- The percentage of dissolved metals from the two glass control panels (GST and GLO) differed from each other by more than 10% for all the metals except zinc.

Table 34. Average ratios of dissolved metals concentrations to total metals concentrations in runoff as a percentage.

Metal	**Steep-Slope Panel**								**Low-Slope Panel**							
	AAR	**AS[A]**	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**	**GST**	**BUA**	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
Arsenic	108	101	*	97	107	*108*	79	117	*	*96*	90	*	*98*	79	*	78
Copper	*74*	*76*	*99*	25	*71*	*95*	158	83	411	54	38	32	38	50	46	49
Lead	206	39	65	14	*82*	*	93	68	*	*	*18*	34	60	46	*61*	49
Zinc	*116*	233	224	105	*106*	*110*	*100*	189	273	220	73	*106*	152	149	72	180

[A] Average across three asphalt shingle replicates.

Yellow shading with italicized numbers indicates the RSD is ≤ 15% among the three rain events compared.

Dark gray shading indicates glass control panels.

* Total metals below MDL for one or more sample(s); percent not calculated.

Panel identification codes are defined in Table 2 on page 40.

For those metals detected at very low concentrations, the dissolved metals concentrations were frequently substantially greater than 100% of the total metals concentrations. In some instances, the percentages of dissolved metals were substantially higher than 100%. Ecology decided to present average values in Table 34 to dampen the effects of this variability. The high variability of the percentages may be attributable to a number of factors including:

- The MDLs for the dissolved metals are lower than for the total metals, allowing greater sensitivity for the dissolved fraction.
- Generally, where percentages were substantially greater than 100%, concentrations of both dissolved and total metals were very low. At low concentrations, small differences in concentration can have a large impact on the dissolved to total metals ratios.
- Some contaminants may have arisen from the filters themselves. Filter blanks were not analyzed.

The traditional comparison of dissolved to total metals concentrations as a percent appears to be a useful tool in understanding the dynamics of these two analyses only for those metals and roofs that released metals concentrations much greater than the reporting limit. The value of conducting dissolved metals analyses in future studies needs to be reconsidered.

PAHs

PAHs are stable multi-ring compounds that tend to degrade slowly. Many of them are considered persistent, bioaccumulative, or toxic compounds (PBTs) in Washington. Appendix H presents background information about sources and environmental impacts of PAHs

The specific PAH compounds detected in roof runoff and their concentrations exhibited great spatial variability between adjacent roofs of like composition. This variability likely relates to the heterogeneity of aerial deposition. It could also be related to the ability of the laboratory instrumentation to detect the compounds and quantify the concentrations.

Similar types of PAH compounds were generally detected from the steep- and low-slope panels. The treated wood shake (TWO) and wood shingle (WOS) panels had the fewest number of PAHs detected in the runoff, while the two glass control panels (GST and GLO) had the greatest numbers of detected compounds. The modified built-up roof with the SBS cap sheet (BUS) and EPDM panels had the greatest number of detections across the most rain events. The BUS panel had multiple detections of 1- and 2-methylnaphthalene and phenanthrene. The BUS roof differed in number of compounds and detection from both of the other two panels of built-up roofing materials. PAHs detected in runoff from the BUS panel were similar in number but different in composition to those detected on the asphalt shingle panels.

To assess the overarching results of the PAH analyses and reduce the impacts of the spatial heterogeneity and low concentrations of various compounds, staff calculated the sums of the PAH compounds for each roof type and each rain event, as presented in the *Results* section. Table 35 presents the results of the calculations as medians. Although statistical analyses were not conducted because of the limited number of samples for many of the roofs, the median concentrations of total detected PAHs in runoff from the roofs tested are not apparently different than the glass control panels. The highest value for the steep-slope glass control panel (0.087 ug/L) was greater than the 50th percentile (median value) for the other steep-slope roofs. Likewise the highest value for the low-slope glass control panel was near the median values for the other low-slope roof. The data suggest that the new roofing materials assessed in this study do not release PAHs to runoff. The impacts of roof aging on chemicals that leach from the roofing materials have not yet been assessed.

Table 35. Median concentrations of the sum of detected PAHs (in ug/L) in runoff by panel.

Steep-Slope Panels								Low-Slope Panels							
AAR	**AS[A]**	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**	**GST**	**BUA**	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
0.02	0.02	0.05	0.03	0.04	0.03	0.05	0.04	0.01	0.01	0.07	0.08	0.03	0.01	0.03	0.04

[A] Based on average of three replicate asphalt shingle panels.
Shading indicates glass control panel.
Panel identification codes are defined in Table 2 on page 40.

Comparison of PAHs to Aerial Deposition Measured in the Puget Sound Region

Brandenberger et al. (2010) measured aerial deposition of certain compounds in the Puget Sound region. Specifically, they assessed the fluxes of those PAH compounds that are carcinogens. Concentrations of carcinogenic PAHs from the glass control panels were used to calculate fluxes to compare with fluxes measured by Brandenberger et al. (2012). For this study, Ecology calculated the median, minimum, and maximum flux values for those rain events for which antecedent dry periods exceeded one hour. Table 36 compares the values calculated from data from this study with ranges found by Brandenberger et al. (2012) for four stations in the southern Puget Sound region.

Table 36. Comparison of carcinogenic PAH fluxes ($ng/m^2/d$) with results of Brandenberger et al. (2012).

Surface	Median	Minimum	Maximum
Glass steep slope (GST)	196	150	4,435
Glass low slope (GLO)	226	159	3,754
Brandenberger et al. (2012) (measured ranges)	11.6 - 238	1 - 52	31 – 1,490

Data for the glass control panels were near the upper end of the range of median values for the four stations in southern Puget Sound. Both the minimum and maximum values calculated from this study were clearly higher than those recorded for the Tacoma Commencement Bay station of the Brandenberger et al. (2012) study. However, this is not surprising since the methodology of this study was not designed to measure these fluxes, and the length of the monitoring period was much shorter than the 10- to 21-day collection periods used in the Brandenberger et al. study. Ecology's substantially shorter collection period likely resulted in spurious flux estimates. Clearly Ecology's plot-scale roofing assessment was not designed for these purposes.

Phthalates

Phthalate esters are widely used industrial chemicals which impart flexibility to polyvinyl chloride (PVC) resins (Staples et al., 1997). Background information about sources and environmental impacts of phthalates is provided in Appendix H.

Generally, concentrations of detected phthalates were low across all roofs. (See Appendix D for analytical results.) Table 14 (page 69) in the *Results* section lists the specific phthalates measured above the laboratory contaminant threshold and the numbers of rain events during which each compound was detected. The reduced frequency in Events 5 through 10 may be an artifact of the fact that phthalate concentrations in the method blanks gradually increased over the duration of the project.

As with the PAHs, Ecology calculated the median values of the sum of the detected phthalate compounds (Table 37). The phthalates were not detected, or not detected at concentrations above the glass control panels, except for the treated wood shake roof (TWO). With this exception, it appears that phthalates are not likely contaminants leaching from the new roofing materials evaluated in this study. Phthalates measured in runoff from new roofing materials were near the ability of the method to quantify them and likely represent background conditions.

Table 37. Median concentrations of the sum of the detected phthalates (in ug/L) by panel.

Steep-Slope Panels							
AAR	**AS**[A]	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**	**GST**
ND	0.43	0.57	ND	0.24	4.20	0.85	ND
Low-Slope Panels							
BUA	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
0.25	0.20	0.20	0.22	0.44	ND	ND	0.48

[A] Based on average of three replicate asphalt shingle panels.
ND: Not detected at the method detection limit (MDL)
Shading indicates glass control panels.
Panel identification codes are defined in Table 2 on page 40.

The treated wood shake roof (TWO) had concentrations of phthalates above 1 ug/L during all three rain events for which phthalates were measured on this roof. These concentrations were largely attributable to elevated concentrations of bis (2 ethyl hexyl) phthalate (DEHP). Levels of DEHP were much higher than any of the other phthalates and were found repeatedly on the CCA treated wood shake roof runoff only.

Since the amount of DEHP was low, it is likely that the compound was introduced to the cedar shakes during the manufacturing or transportation process. Representatives of the wood shake and shingle industry on the Roofing Task Force were not aware of sources of DEHP in the manufacturing processes. A subsequent literature review revealed that industrial hydraulic, vacuum pump, and lubricating oils can be a potential source of DEHP (EPA, 2013). These may be used in the pressure treatment process of wood products. Ecology should consider testing the treated wood shake roof (TWO) for phthalates in the future to monitor possible declines in the DEHP concentration with time.

PBDEs

PBDEs are semi-volatile compounds that belong to a broad class of brominated chemicals used as flame retardants. PBDEs sorb to small particles, such as dust, and are transported with the particles and are frequently found in measurements of aerial deposition. Background information about sources and environmental impacts of PBDEs is provided in Appendix H.

PBDEs are added to products so they will not catch fire or will burn more slowly if exposed to flame. PBDEs have been added to plastics, upholstery fabrics, and foams that are incorporated into products such as computers, TVs, furniture, and carpet pads (Ecology, 2006). They may also have been added to roofing materials and or coatings.

In this study, PBDE congeners were detected rarely and only at concentrations less than the reporting limit (RL). As with the PAHs and phthalates, Ecology summed the PBDE congeners that were detected by roof type. These are presented in the *Results* section (Tables 17 and 18 on pages 74-75). Ecology did not calculate the median of those detections because of the relatively few data points.

Ecology compared PBDE concentrations in runoff from the glass control panels to those from the roofs and found that the roof concentrations were not outside of the range of the glass control panels. The new roofing materials in this study do not appear to be leaching PBDEs to the runoff. The PBDEs detected in the runoff are likely a result of spatially heterogeneous aerial deposition. The impact of aged roofing materials cannot be determined from this study.

SPLP Analysis

Utility of SPLP Analysis

Ecology used the Synthetic Precipitation Leaching Procedure (SPLP) analysis to assess the effectiveness of specific coatings in reducing zinc or copper leaching from metal roofing materials. 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. In this study, the median pH values on the two control panels (4.8 for GST and 5.0 for GLO) were similar to the leachate. However, the specific conductance of the rain runoff ranged as high as 19 us/cm and likely provided somewhat higher buffering capacity than the leachate. The more aggressive leachate was evidenced in this study when comparing the SPLP leachate for zinc from Zincalume®, and copper from the copper coupon, to concentrations observed from the roofs (as discussed below).

After conducting the SPLP analysis, Ecology identified two issues which reduced the utility of the SPLP data.

The first issue is related to the thickness of the coatings. Coatings were hand-applied on the galvanized coupons in two thin layers. Some of the coatings were more difficult to apply in a thin layer than others. For example, the Elastuff™ 101 was the most difficult, in part because it dried more slowly than the other coatings and in part because it was very thick. The Poly-Sil® 2500 was applied most heavily based on weight (Table 19 in the *Results* section).

Ecology measured the thickness of the coatings after the leaching analyses. Table 38 lists the post-testing thicknesses along with the manufacturer's recommended application thicknesses. While Ecology staff applied two coats, it is clear from comparisons in the table that staff did not apply the coatings to the prescribed thicknesses. Thus the effectiveness of the coatings at preventing zinc from leaching may not have been reduced to the degree anticipated by the manufacturers.

Second, upon examination of the coupons after the leaching process, the coatings were clearly physically damaged from the rigors of the tumbling and leaching procedure. The laboratory described the SPLP procedure as follows:

> *Coupons were placed with the extraction fluid in glass TCLP vessels. The vessels were then capped and placed on the TCLP tumbler at 30 ±2 rotations per minute for approximately 18 hours. The TCLP tumbler rotates the vessels end over end for the entire 18 hours* (Momohara, 2013).

Table 38. Post-leaching coating thicknesses.

Coating ID	Average Thickness (mils)	Manufacturer Recommended Thickness (mils)	Difference (mils)	Difference (mm)
SNO	3.35	13	-9.65	-0.25
ASW	2.69	5	-2.31	-0.06
ESW	4.27	19	-14.73	-0.37
SIL	9.25	18	-8.75	-0.22
ALA	4.53	16	-11.47	-0.29
EPB	6.27	12.8	-6.53	-0.17
COR	NA	NA	NA	NA
SYN	NA	1	NA	NA

NA: Not available as the coupons were coated by the industry.
Coating ID codes are defined in Table 3.

Figure 16 provides photographs of representative post-testing coupons.

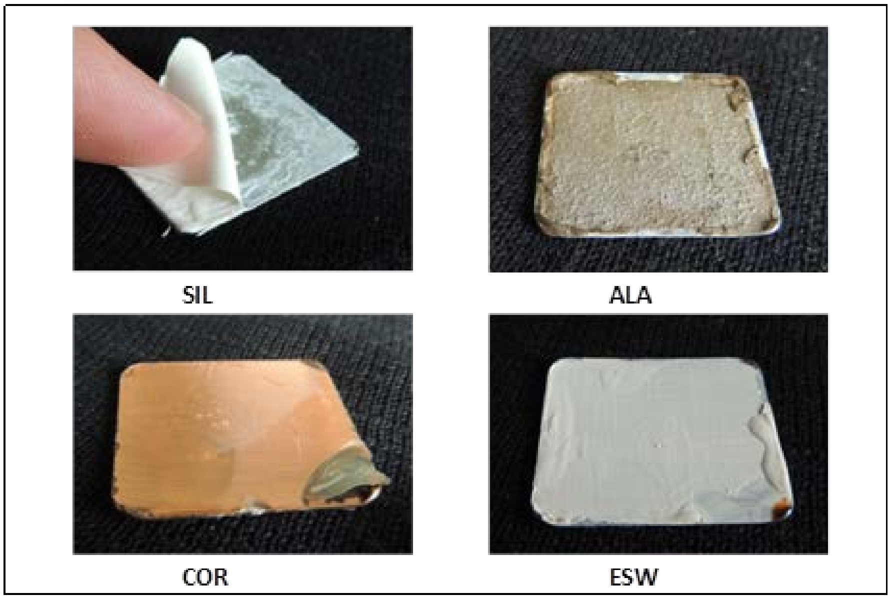

Figure 16. Photographs representative of post-leached coupon condition.

To better simulate leaching to precipitation, at least two modifications to the procedure may be useful. First, the leachate should be modified to reduce the acidity and increase buffering capacity. A synthetic rain similar in chemical composition to local rain could be developed. Second, based on the physical damage of the test to the coupons, a less rigorous mixing protocol should be followed to prevent coating from being removed. Mixing could include placement of the containers with the coupons on a shaker table set to rotate relatively slowly. Third, alternative leaching methods and procedures could be assessed. For example, Taylor (2004) applied the leachate using spray bottles.

Despite the shortcomings of the SPLP test, the following two sections describe the findings for metals and organics found in the leachate.

Metals

Ecology used the SPLP analysis to assess the effectiveness of specific coatings in reducing zinc or copper in the leachate. The SPLP also assessed the relative difference between zinc leached from galvanized metal and zinc leached from the Zincalume®. Ecology is able to make the following statements:

- The SPLP analysis revealed that Zincalume® coupons released, on average, 56% less zinc than the galvanized steel.
- All coatings resulted in some reduction of zinc or copper in the leachate.
- Concentrations of other metals (arsenic, cadmium, copper, and lead) in the leachate were near or below the MDL.

To understand potential bias for thicker applications, Ecology graphed coating weight applied to the galvanized coupons (except for Poly-Sil® 2500) and found that the thicker the coating (weight), the better reduction in zinc leached. Figure 17 shows a linear regression coefficient (r^2) of 0.94, without the Poly-Sil® data included. This correlation is not surprising as Heinje (pers. comm., 2013), a member of the Roofing Task Force, reported that the percent metal reduction by a coating is a function of the square of the thickness of the coating. The results indicate that, for most of the coatings evaluated, thicker layers would better reduce the zinc leaching to runoff.

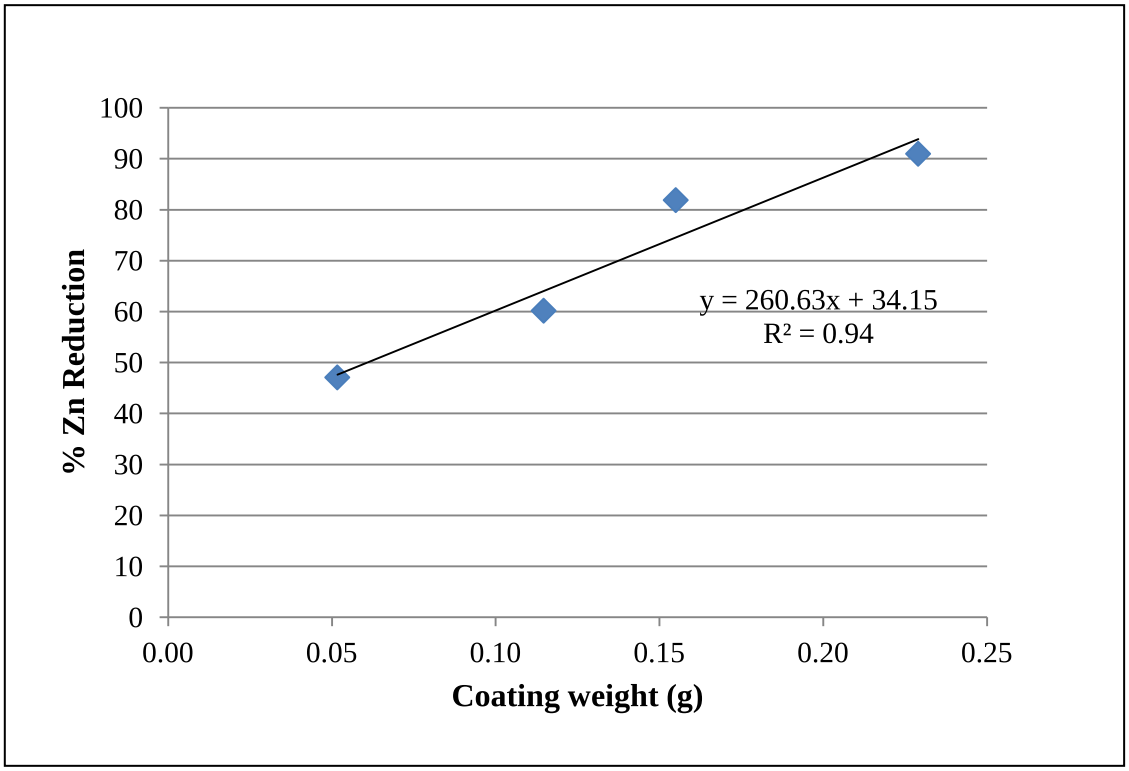

Figure 17. Relationship between coating weight and reduction in zinc concentration.

Coatings applied to the copper coupons also reduced the amount of copper leached during the SPLP procedure. Because the Copper Development Association (CDA) applied the coatings, their thicknesses are assumed to be similar to one another, indicating the Syncrylac® provided greater reduction in the release of copper.

Ecology compared zinc and copper released from the Zincalume® (ZIN) and copper (CPR) roofing panels to releases from the coupons exposed to the SPLP procedure. These were standardized for surface area and average annual precipitation. For the Zincalume® and copper panels, these calculations resulted in values of 0.54 ug zinc/yr cm^2 and 7.09 ug copper/yr cm^2 for the Zincalume® and copper, respectively. Metals leached during the SPLP test from the uncoated Zincalume® and copper coupons were much higher at 42.1 ug zinc/yr cm^2 and 43.1 ug copper/yr cm^2. The results indicate that the slightly greater buffering capacity of rain reduces the metals leaching. These results also suggest that the SPLP test, as used in this study, should not be used to simulate runoff from roofing materials.

Organics

Ecology also evaluated PAHs and phthalates released from all coupons, as well as PBDEs, from the three Elastuff™ 101 coupons, to assess whether other compounds (potentially more toxic to the environment) were released from the coatings.

Table 21 (*Results* section) shows PAH compounds detected in leachate from the coupons. Anthracene, fluorene, naphthalene, and pyrene were each detected in the leachate from only one coupon. Both 1- and 2-methylnaphthalene were detected one or more times on all but the Syncrylac® and Coraflon® coupons. Phenanthrene was detected consistently in leachate from the Karnak coated coupons. The asphalt-based Karnak® Fibered Aluminum Asphalt Coating 98AF (ALA) had the greatest number of PAH compounds detected.

Table 39 shows the sums of the detected PAHs detected by coating type. The two coatings on the copper coupons released the lowest concentrations of total PAHs. Of the coatings applied to the galvanized zinc coupons, Elastuff™ 101 released the highest concentrations of total detected PAHs.

Only one sample had any phthalates detected; leachate from the EPB-03 sample had diethyl phthalate at 0.28 ug/L. Also only one coupon had a detectable level of PBDEs; leachate from the EPB-06 sample was reported at an estimated concentration of 0.01 ug/L for the PBDE-209 congener. As indicated above, the PBDE-209 congener is associated with deca-BDE. Because only one of the three replicates of the Elastuff™ 101 showed concentrations of either the phthalate or PBDE, the study cannot conclude that this coating leaches either of these compounds consistently.

Table 39. Average of the sum of detected PAHs by coating type.

Coating	Coupon Code	PAHs (ug/L)
Galvanized steel coated with Snow Seal (Ames Research Laboratories)	SNO	0.017
Galvanized steel coated with SHER-CRYL™ HPA High Performance Acrylic Semi-Gloss Coating (Sherwin Williams)	ASW	0.078
Galvanized steel coated with UNIFLEX® Elastomeric Roof Coating (Sherwin Williams)	ESW	0.003
Galvanized steel coated with Poly-Sil 2500 High Solids (Coatings & Foam Solutions)	SIL	0.060
Galvanized steel coated with Karnak® Fibered Aluminum Asphalt Coating 98AF	ALA	0.077
Galvanized steel coated with Quest Construction Products Elastuff™ 101	EPB	0.178
Copper coated with Syncrylac®	SYN	0.001
Copper coated with PPG Architectural Finishes Coraflon® ADS Intermix	COR	ND

ND: not detected

Review of MSDSs for Coatings

Ecology conducted a cursory review of the material data safety sheets (MSDSs) for coatings used for this study to ascertain whether other potentially toxic substances were part of the formulations. (Appendix I contains copies of the MSDSs.) The review was conducted using the Pharos database[2], the GreenScreen^{TM} List Translator provided by Healthy Building Network. Pharos lists chemicals identified by authoritative bodies as having different degrees of concern. Using Pharos, identification of a high level of concern for a specific chemical is indicative of potential problems associated with the use of this chemical. If the chemical is not identified in Pharos, however, further review is necessary and the chemical cannot be assumed to be a safe alternative.

The potentially hazardous constituents in each of the coatings are listed in Table 40 by product. Only the Poly-Sil® 2500 reported no toxic constituents. However, these results should not be considered indicative of potential toxicity concerns associated with all alternatives. MSDSs are primarily used to protect worker health and safety and may not include all chemical constituents that have long-term impacts on human health and the environment.

Before recommending any of these coating products to prevent copper or zinc leaching in stormwater, a thorough alternatives assessment should be conducted, emphasizing hazard assessment using the GreenScreen^{TM} methodology and including all pertinent life-cycle impacts.

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[2] Pharos database available at: http://www.pharosproject.net/material/, accessed 9/2013.

Table 40. List of potentially hazardous compounds found in coating products.

Compound	**CAS #**	**Carcinogenicity**	**Mutagenicity**	**Acute Aquatic Toxicity**	**Acute Mammal Toxicity**	**Endocrine Activity**	**Reproductive Toxicity**	**Developmental Toxicity**	**Respiratory Sensitization**	**Persistence**
Ames Research Laboratories Snow Seal										
Acrylic-styrene polymer		NA	NA	NA	NA	NA	NA	NA	NA	
Styrene monomer	100-42-5	Yes	Some	Some	Some	Some	Yes		Some	
Sherwin Williams SHER-CRYL™ HPA High Performance Acrylic Semi-Gloss Coating										
2-(2-Methoxy ethoxy) ethanol	111-77-3						Yes	Some		
Sherwin Williams UNIFLEX® Elastomeric Roof Coating										
Mineral spirits	64742-88-7				Some					
Parachlorobenzo-trifluoride	95-56-6	NA	NA	NA	NA	NA	NA	NA	NA	Yes
Acetone	67-64-1									
Poly-Sil 2500 High Solids										
NA										
Karnak® Fibered Aluminum Asphalt Coating 98AF										
Aliphatic hydrocarbons (Stoddard solvent)	8052-41-3	Yes	Yes	Some	Some					
Aromatic petroleum distillates	64742-95-6	Yes	Yes		Some					
Aluminum-based pigment	7429-90-5				Some	Some			Some	
Quest Construction Products Elastuff™ 101										
Xylene	1330-20-7			Some	Some	Some	Yes			
Ethylbenzene	100-41-4	Yes		Some	Some		Yes			
Chlorinated paraffin waxes	63449-39-8	Some		Some		Some				Yes
Antimony oxide	1309-64-4	Yes			Some					
Arsenic compounds	7440-38-2	Yes	Some	Some	Some	Some	Yes	Some		
Lead compounds	7439-92-1	Yes	Some	Some	Some	Some	Yes	Yes		
PPG Architectural Finishes Coraflon® ADS Intermix										
Parachlorobenzo-trifluoride	95-56-6	NA	NA	NA	NA	NA	NA	NA	NA	Yes
Xylene	1330-20-7			Some	Some	Some	Yes			
Ethylbenzene	100-41-4	Yes		Some	Some		Yes			
Syncrylac®										
Toluene	108-88-3			Some	Some		Yes	Yes		

Yes: Significant concerns identified by at least one authoritative body. Likely to be a Benchmark 1 chemical (i.e., a chemical to avoid) using the GreenScreen^{TM}.

Some: Some concerns and may be a Benchmark 1 chemical. Further review necessary.

NA: No data available. Toxicity not evaluated by authoritative bodies. Further review necessary.

Conclusions

The Department of Ecology (Ecology) evaluated runoff from 18 constructed pilot-scale roof panels (4 feet by 8 feet). The panels represented included 14 types of roofing materials, two replicates of the asphalt shingle roofing material, and two glass control panels. With input from the Roofing Task Force (RTF), roofing materials selected for testing represented the most commonly used roofing types in the Puget Sound basin (Appendix B in Ecology, 2011a) as well as other roofing materials recommended by the RTF. Ecology staff collected runoff following 10 rain events from February through April 2013.

Comparisons of concentrations of metals in runoff from the roofing panels in this study with concentrations used to estimate releases in the Puget Sound Toxics Assessment (Ecology, 2011a) revealed that, for every metal and every roofing material evaluated (except copper in runoff from a copper panel and arsenic in runoff from the asphalt shingle panel with algae resistance), concentrations used in the Puget Sound Toxics Assessment ranged from two-fold to two orders of magnitude higher than those found in the present study. However, runoff concentrations used to estimate releases in the Puget Sound Toxics Assessment were predominantly based on whole roofing systems, rather than roofing materials alone.

- Based on the data collected, the roofing materials on the panels tested released low concentrations of total metals in runoff, with the following exceptions:
    - The treated wood shake panel (TWO) was treated with chromated copper arsenate (CCA), and met the substantive portions of the best management practices (BMPs) prescribed by the Western Wood Preservers Institute (WWPI). This panel released concentrations of arsenic (692 to 4,690 ug/L) and copper (601 to 3,190 ug/L). The arsenic and copper concentrations were significantly higher than concentrations from the glass control panels. The treated wood shake panel also released low, but significantly higher, concentrations of cadmium than the glass control panel.
    - The new PVC panel released concentrations of arsenic in runoff that ranged from 22 and 117 ug/L. These were significantly higher than the arsenic concentrations in the runoff from the glass control panels. Arsenic likely serves as a biocide in the PVC matrix.
    - The copper panel (CPR) released concentrations of copper that ranged from 1,035 to 3,380 ug/L and were significantly higher than from the glass control panel.
    - The asphalt shingle panel with algae-resistant (AR) (AAR) and the asphalt shingle panels without AR (AS^{A}) also released copper concentrations significantly higher than the glass control panel, although these concentrations were one to two orders of magnitude lower than those from the copper roofing panel.
    - The Zincalume® (ZIN) and ethylene propylene diene monomer (EPDM) panels released concentrations of zinc significantly higher than those from the low-slope glass control panel (GLO). Zinc represents one of two metals in the Zincalume® alloy. Zinc is used as a catalyst in manufacturing EPDM.
    - The painted galvanized metal (PAZ), treated wood shake (TWO), wood shingle (WOS), and asphalt shingle with AR (AAR) panels released concentrations of zinc that were

significantly higher than concentrations from the glass control panel. However, zinc in the runoff from these panels was up to an order of magnitude lower than zinc released from the Zincalume® (ZIN) and EPDM panels.

  - The steep-slope glass control panel (GST) released concentrations of lead that were significantly higher than from the treated wood shake panel (TWO). The reason for this difference can only be speculated.

- Where metals concentrations were high, the percentages of dissolved metals represented the majority of the metals in the runoff (between 70% and slightly more than 100%).
- Concentrations of PAHs in runoff from the new roofing panels were low and not distinguishable from concentrations from the glass control panels, even in those roofs which have asphalt components (such as asphalt shingle and built-up roofing).
- Concentrations of phthalates in runoff from the new roofing panels were low. For all but one type of roofing panel, phthalates were not distinguishable from the glass control panels. The only exception, the treated wood shake panel (TWO), had detectable bis (2-ethyl hexyl) phthalate concentrations. These may have originated during the pressure treatment process.
- Concentrations of PBDEs in runoff from the new roofing panels were low and not distinguishable from concentrations from the glass control panels.

The following conclusions can be drawn from the Synthetic Precipitation Leaching Procedure (SPLP) analysis of galvanized steel and copper coupons (samples) with and without various coatings:

- While the coatings were damaged in the SPLP tumbling procedure, all coatings of the metal coupons reduced the concentrations of zinc or copper released from the zinc and copper coupons, respectively; coatings reduce zinc concentrations in the leachate between 47 and 91%. In general, the thicker the coating, the greater the zinc reduction realized.
- Low levels of PAHs were detected leaching from the coatings, but these were at concentrations generally less than 0.1 ug/L. The Karnak Fibered Aluminum 98AF® coating released the greatest numbers of PAH compounds, while the Elastuff™ 101 released the highest concentration of total PAHs.
- One phthalate and one PBDE congener were detected leaching from the Elastuff™ 101 coating in only one of the replicates. Based on a single detection, Ecology did not conclude that Elastuff™ 101 releases these compounds.
- Ecology compared the release of zinc and copper from the Zincalume® (ZIN) and copper roofing panels (CPR) exposed to precipitation to that of the uncoated Zincalume® and copper coupons exposed to the SPLP test. For the Zincalume® and copper panels, these calculations resulted in releases of 0.54 ug zinc/yr cm^2 and 7.09 ug copper/yr cm^2, respectively. The metals leached from the uncoated Zincalume® and copper coupons in the SPLP leachate resulted in much higher values: 42.1 ug zinc/yr cm^2 and 43.1 ug copper/yr cm^2, respectively. These results suggest that the SPLP test, as used in this study, should not be used to simulate runoff from roofing materials.

Recommendations

Based on the Pilot Study

Concentrations of total arsenic, copper, lead, and zinc were consistently measured in runoff from all of the new roofing materials evaluated. As roofing materials age, concentrations of metals released may change over the life of a roof. Ecology recommends that the impacts of aging on metals release continue to be monitored. Future investigations should continue to assess total metals concentrations. Specifically:

- As the treated wood shake roof (TWO) continues to leach chromated-copper-arsenate (CCA), concentrations of arsenic and copper may diminish. The impacts of roof aging on the release of these two metals should be monitored on a routine basis.
- Because concentrations of total cadmium and lead in runoff from all of the roofs were very low, future sampling for cadmium and lead could be reduced in frequency.
- Total copper and zinc should continue to be monitored in runoff from all the roof materials.
- Future monitoring should consider a full suite of total priority pollutant metals for at least one rain event. Future monitoring needs should be assessed based on the results.
- Based on the XRF findings of elevated chromium in the treated wood shake coupons (samples) and the painted galvanized metal coupons, future studies should consider monitoring chromium in runoff from these two roofing materials.

Given the disparity between the total and dissolved metals measurements, and given that metals may change between particulate and dissolved phases depending on pH of the media, Ecology recommends measuring total metals for most of the roofs and dissolved metals only for those roofs where concentrations are elevated.

While the new roofing materials evaluated in this study do not appear to be leaching substantial concentrations of organics (with the exception of the treated wood roof), organics may become more leachable as the roofing materials age. The impact of aging on the release of PAHs, phthalates, and PBDEs from roofing materials should be evaluated, but at less frequent intervals. Future testing of the treated wood shake roof (TWO) should include sampling for phthalates more routinely.

The results collected in this pilot study do not provide Ecology with a long enough period of record to have confidence in making decisions about future actions related to assessing roofing materials or whether source control actions are needed for the materials tested. Ecology determined that a robust baseline from a single location over a one-year period would better serve the on-going studies of these roofing panels. To that end, Ecology continued sampling runoff from the roofing panels for another 10 rain events in the fall and winter of 2013/2014. The Addendum to the Quality Assurance Project Plan (Ecology, 2013b) describes the parameters sampled for and the frequency of monitoring. The additional data collection will provide greater statistical power in discerning differences between roofing materials and changes over time.

Based on SPLP Testing

Ecology's intent in conducting the Synthetic Precipitation Leaching Procedure (SPLP) portion of the study was to determine (1) the effectiveness of the coatings at reducing metals leaching to simulate precipitation, and (2) whether coatings could leach organic contaminants, thereby exchanging release of one toxic compound for another toxic compound and not necessarily achieving environmental benefit. More work is needed in this area.

To better simulate precipitation, the SPLP leachate should be substantially modified. The leachate should better simulate rain with reduced acidity and higher buffering capacity. Further, based on the physical damage of the test to the coupons, a less rigorous mixing protocol should be followed to prevent coating from being removed. A custom SPLP-like method should be developed to better mimic precipitation runoff and reduce costs of larger scale testing.

Before recommending any of the coatings assessed in this study, the coatings should undergo a thorough alternatives assessment, emphasizing hazard assessment, using the GreenScreen™ methodology and including all pertinent life-cycle impacts.

Long-Term

At the initiation of this study, Roofing Task Force (RTF) members recognized additional variables that merit study. These variables were not included in the initial study because of the limitations of available resources. Listed below are those issues and variables identified by the RTF as needing further evaluation:

- Given that even the highest zinc concentrations in runoff from the Zincalume® (ZIN) and EPDM roofs were an order of magnitude lower than the mean concentrations used by Ecology to asses sources of contaminants in Puget Sound from roofing systems (Ecology, 2011a), other components of roofing systems (e.g., flashings, downspouts, gutters, HVAC) should be evaluated to assess releases of metals to stormwater runoff.
- The roofing materials assessed in this study should be evaluated over their life span to determine whether contaminants leach in greater or lesser amounts as roofs age. Such an assessment could be continued at intervals at the Washington Stormwater Center, where the roofing panels will be re-located.
- Based on concentrations of metals and organics released in this study, the fate, transport, and toxicity of contaminants after they leave the roofing materials should be assessed to determine under what conditions these contaminants could adversely affect the quality of receiving waters.
- As vegetated roof systems become more popular in the Puget Sound basin, runoff/run-through from their components (e.g., underlayments, barrier systems, and soil matrices) should be assessed for both concentrations and releases of contaminants and compared to the results of this study.

- The leachability of biocides and chemicals used as flame retardants from roofing materials should be evaluated.
- The impacts to stormwater of “after-market products” should be assessed. These are products that building owners or their contractors apply to roofing materials for maintenance and repair. These include products such as algae/moss removal treatments, post-manufactured treatments or coatings, adhesives and seaming tapes used for repair.

  The RTF noted that Ecology should not develop policy that could eliminate constituents from the manufacture of roofing materials but subsequently require greater maintenance with application of products that result in greater environmental harm.

  To assess whether an “after-market product” should be eliminated because it is not needed or whether the product’s chemical make-up should, or can be, modified to cause less environmental and human health impacts, a thorough alternatives assessment should be conducted. The alternatives assessment should emphasize hazard assessment using the GreenScreen™ methodology and include all pertinent life-cycle impacts.

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Glossary, Acronyms, and Abbreviations

Glossary

Atmospheric deposition: Atmospheric deposition is the result of airborne chemical compounds settling onto the land or water surface.

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

Conductance: A measure of water's ability to conduct an electrical current. Conductance is related to the concentration and charge of dissolved ions in water.

Congener: In chemistry, a PBDE congener is any single, unique well-defined chemical compound in the PBDE category. The name of a congener specifies the total number of chlorine substituents and the position of each chlorine.

Constituent: A part of a whole, generally chemical elements or compounds which are used to formulate a product or describe the quality of water.

Coupon: A term used in the roofing industry to mean a small sample of roofing material.

Leachate: A solution formed by leaching of soluble contaminants into a liquid, such as rain or synthetic precipitation.

National Pollutant Discharge Elimination System (NPDES): National program for issuing, modifying, revoking and reissuing, terminating, monitoring, and enforcing permits, and imposing and enforcing pretreatment requirements under the Clean Water Act. The NPDES program regulates discharges from wastewater treatment plants, large factories, and other facilities that use, process, and discharge water back into lakes, streams, rivers, bays, and oceans.

Organics: Carbon-based organic compounds in this study include PAHs, phthalates, and PBDEs.

Parameter: One of a set of measurable factors, such as temperature, pH, specific conductance, and water chemistry, that define water quality. (Synonymous with constituent or analyte.)

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 10 times more basic than one with a pH of 7.

Phthalate: An organic chemical compound widely used in industry to impart flexibility to polyvinyl chloride resins, a plasticizer.

Pollution: Contamination or other alteration of the physical, chemical, or biological properties of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will, or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

Puget Sound basin: All the freshwater bodies within the 12-county watershed that ultimately flow into the waters of Puget Sound and the Strait of Juan de Fuca.

Runoff: Runoff is the overflow of water from the land and into a body of water.

Specific conductance: A measure of water's ability to conduct an electrical current. Specific conductance is related to the concentration and charge of dissolved ions in water.

Storm: In this study, *storm* is synonymous with *rain event*.

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

Surface waters of the state: Lakes, rivers, ponds, streams, inland waters, salt waters, wetlands and all other surface waters and water courses within the jurisdiction of Washington State.

50th percentile: A statistical number obtained from a distribution of a data set, above which 50% of the data exist and below which 50% of the data exist.

Acronyms and Abbreviations

APP	Atactic polypropylene roofing
AAR	Asphalt shingle roof without algae resistant copper-containing granules
AR	Algae-resistant
AS^A	Asphalt shingle roofs, the average of the three replicates
BUA	Modified built-up roof with APP granulated cap sheet
BMP	Best management practice
BMS	Building Materials Specialist
BUR	Built-up roof
BUS	Modified built-up roof with SBS granulated cap sheet
CCA	Chromated-copper-arsenate
CPR	Copper roof
CTI	Concrete tile roof
DBP	Di-n-butyl phthalate (DBP)
DEHP	Bis (2-ethylhexyl) phthalate
DI	Distilled, deionized

DIDP	Diisodecyl phthalate
DINP	Diisononyl phthalate
EAP	Environmental Assessment Program
Ecology	Washington State Department of Ecology
e.g.	For example
et al.	And others
EPA	U.S. Environmental Protection Agency
EPDM	Ethylene propylene diene monomer
GLO	Glass control roof, low slope
GST	Glass control roof, steep slope
HDPE	High density polyethylene
HVAC	Heating, ventilation, and air conditioning
ID	Identification
i.e.	In other words
LOD	Limit of detection
MDL	Method detection limit
MEL	Manchester Environmental Laboratory
MS	Matrix spike
MSD	Matrix spike duplicate
MSDS	Material Safety Data Sheet
NADP	National Atmospheric Deposition Program
PAH	Polycyclic aromatic hydrocarbon
PAZ	Painted galvanized steel roof
PBDE	Polybrominated diphenyl ethers
PBT	Persistent, bioaccumulative, and toxic substance
PCB	Polychlorinated biphenyls
PVC	Polyvinyl chloride
QA	Quality assurance
QC	Quality control
RL	Reporting limit
RSD	Relative standard deviation
RTF	Roofing Task Force
SPLP	Synthetic Precipitation Leaching Procedure
SPRI	Single Ply Roofing Institute
SBS	Styrene butadiene styrene
TPO	Thermoplastic polyolefin roofing
TWO	Treated cedar shingle roof, treated with CCA
WOS	Cedar shingle roof
WWPI	Western Wood Preservers Institute
XRF	X-ray fluorescence
ZIN	Zincalume® roof

Units of Measurement

°C	degrees centigrade
cm	centimeters
ft	feet
ft^2	square feet
g	gram, a unit of mass
in	inches
kg	kilograms, a unit of mass equal to 1,000 grams
m	meter
m^2	square meters
mg/L	milligrams per liter (parts per million)
mil	0.001 inch
mL	milliliters
mm	millimeter
mm^2	square millimeters
mm/hr	millimeters per hour
ng	nanograms
s.u.	standard units
ug/L	micrograms per liter (parts per billion)
uS/cm	microsiemens per centimeter