Roofing Materials Assessment

Investigation of Toxic Chemicals in Roof Runoff from Constructed Panels in 2013 and 2014

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Roofing Materials Assessment

Investigation of Toxic Chemicals in Roof Runoff from Constructed Panels in 2013 and 2014

by

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Abstract

The Washington State Department of Ecology (Ecology) collected data on contaminants in roof runoff from newly installed roofing materials during 10 rain events between February and April 2013 (Round 1). To improve characterization of baseline conditions and begin to evaluate effects of weathering, Ecology collected a second round of data during 10 rain events between October 2013 and January 2014. In both rounds, Ecology analyzed runoff collected from 18 constructed roofing panels for metals (arsenic, cadmium, copper, lead, and zinc) and organic compounds. Ecology reported the results of Round 1 sampling in February 2014. This report presents the results of Round 2 sampling and compares the results from the two rounds.

Ecology identified significantly higher concentrations of one or more of the five metals in runoff from several roofing panels when compared to the glass control panels. Most notably, the following roofing panels released the highest metals concentrations: treated wood shakes released arsenic and copper, copper released copper, PVC released arsenic, and Zincalume® and EPDM released zinc. Comparisons of concentrations in runoff from the roofing panels during Round 1 with concentrations during Round 2 identified significant reductions in metals concentrations in runoff from many of the panels within the year of panel aging.

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

Comparing metals concentrations in runoff from this study with concentrations used to estimate releases to the Puget Sound basin in Ecology’s 2011 study, Ecology found, with one exception, that concentrations used in the 2011 study ranged from 30% to three orders of magnitude higher. However, the 2011 study estimates primarily reflect full-scale roofing systems, rather than the single component in this study: roofing materials. Because concentrations in runoff depend on a number of factors – such as roofing materials and components, age of the materials, angle of roof installation, and climatic conditions – comparison of runoff concentrations from individual components to basin-wide releases should be undertaken cautiously.

Ecology recommends:

- Evaluating the impacts of roof aging on the long-term release of toxic chemicals.
- Assessing toxic releases from other roofing system components.
- Evaluating the fate and transport of contaminants and treatment options.
- Assessing after-market roof maintenance products.
- Evaluating toxic releases in runoff from full-scale roofing systems.

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Funding

National Estuary Program (NEP) funding for this project was provided by the U.S. Environmental Protection Agency (EPA). The Asphalt Roofing Manufacturers Association (ARMA) also graciously provided funding for this study.

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

Sampling and Other Assistance

This project could not have been successfully completed without those who helped with the sampling, analysis, and review. All were Ecology employees or retired Ecology employees when we sampled, except for Lisa Rozmyn, an employee of the Washington Stormwater Center, and Liz Werner, a student at the University of Arizona.

- Joel Bird
- Michael Frieze
- Kyle Graunke
- Tom Gries
- Dean Momohara
- Nancy Rosenbower
- Lisa Rozmyn
- John Weakland
- Leon Weiks
- Liz Werner
- Martin Werner

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- Valerie Partridge
- Donna Seegmueller
- Chuck Springer
- Ted Sturdevant
- Chuck Wilkowski

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

Name	***Representing***
Jeff Jacobs	3M
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Wayne Neumann	3M
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John Ferraro	ARMA
Troy Gamba	Boeing
John White	Boeing
Dan Welch	Bundle Design Studio
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Neil Gresham	EHS Manager - Saint-Gobain
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Heather Trim	Futurewise
Shawn Stanley	IB Roof Systems
Eric Van Genderen	International Zinc Association
David Batts	King County Natural Resources
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Joe Russo	Malarkey Roofing
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Howard Thurston	Northwest EcoBuilding Guild
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Paul Riesebieter	Johns Manville and SPRI

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Renee Ramey	Steelscape
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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 (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 could be 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 the relative importance of roofing as a source of metals and organic compounds to the Puget Sound basin.

To that end, Ecology sought and received funding from the National Estuary Program (NEP) to conduct an assessment of roofing materials in the Puget Sound basin and determine whether roofing materials contribute to releases of toxic chemicals. The pilot project evaluated runoff from 4-by-8-foot, pilot-scale roof panels exposed to precipitation in Lacey, Washington. Members of the Roofing Task Force donated and installed the new roofing materials evaluated. The results of the initial pilot project were reported in *Roofing Materials Assessment: Investigation of Toxic Chemicals in Roof Runoff* (Winters and Graunke, 2014).

Context of the Study

This study assessed stormwater runoff from only one component of roofing systems: roofing materials. Ecology recognizes that roofing systems are complex and include not only the roofing materials but also gutters, 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 toxic chemicals 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. Other roofing system components, as well as post-manufacturing treatments that could contribute contaminants in the Puget Sound basin, need to be assessed separately. Ecology recognizes that where elevated levels of contaminants run off of roofing systems, fate and transport modeling and risk assessments can assist in understanding potential impacts on receiving waters of the Puget Sound basin.

Roofing Task Force Involvement

As part of the pilot study, Ecology convened a Roofing Task Force (RTF) in 2012. The RTF consisted of manufacturers, contractors, and other stakeholders. They collaboratively provided input to the design of this study and assessed the results. 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 that limited the number of variables evaluated. The RTF and Ecology hoped that the roofing panels could be used subsequently to assess the impacts of other factors: for example, the affects of roof aging on runoff quality. The RTF also provided study direction in the development of the Quality Assurance (QA) Project Plan (Ecology, 2013a). Industry representatives on the RTF selected the specific products tested, donated the roofing materials, and provided the installation. The RTF members provided substantial comment in the preparation of *Roofing Materials Assessment: Investigation of Toxic Chemicals in Roof Runoff* (Winters and Graunke, 2014) and provided comment on this report as well.

Round 2 of the Study

Following completion of sampling 10 rain events during 2013 (termed Round 1 of the pilot project), Ecology determined that a more robust baseline was needed. Ecology sought and received funding from the Asphalt Roofing Manufacturers Association (ARMA) and additional funding from NEP to conduct a second round of sampling runoff from 10 rain events (termed Round 2 of the pilot project). This report describes the Round 2 results and makes comparisons with the Round 1 results in order to assess the potential impacts of one year of weathering (aging) of the roofing materials.

For a more thorough description of the background, need for a roofing assessment in the Puget Sound basin, and literature review, the reader is referred to Winters and Graunke (2014).

Methods

Ecology evaluated runoff from 18 constructed pilot-scale roof panels (4 feet by 8 feet) from an additional 10 rain events during this Round 2 study. The panels used in both Rounds 1 and 2 of the study represented 14 different types of roofing materials (with three replicates of the asphalt shingle roofing material) and two glass control panels. With input from the 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.

Manufacturers and associations donated and installed the new roofing materials on 18 4-by-8-foot, pilot-scale roof panels at Ecology headquarters in Lacey, Washington. 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. Nor do the results represent runoff from older roofing materials or from complete, full-scale roofing systems.

Steep-slope roofing panels were installed at a 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) and were exposed to the same precipitation events.

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, treated with chromated copper arsenate (CCA)	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 terpolymer (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.

During Round 2 of the study, Ecology staff collected runoff during 10 rain events between October 30, 2013, and January 30, 2014. Precipitation landing on a panel flowed into a Teflon®-lined removable gutter and into a 63-liter, stainless-steel pot. Samples were obtained from the stainless-steel containers and shipped to the laboratory for analysis. The runoff samples collected during each rain event represented an integration of the water that ran off during the entire monitored event.

During three of the 10 Round 2 rain events, Ecology analyzed all of the following parameters in the runoff:

- Total 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, only total metals were analyzed in the runoff from every panel. Ecology also recorded field parameters including pH, specific conductance, temperature, and volume of the runoff collected.

Findings

With data gathered from a total of 20 rain events (Rounds 1 and 2), Ecology established a baseline of concentrations of metals and organics in runoff from new roofing materials for climatic conditions in the Puget Sound basin. While Ecology found elevated concentrations of metals in runoff from a few of the roofing materials, runoff from the majority of the roofing materials tested was not elevated compared to the control panels. Generally, Ecology found elevated concentrations of copper and arsenic in runoff from the treated wood shake panel (TWO), arsenic in runoff from the PVC panel, copper in runoff from the copper panel (CPR), and zinc in runoff from the Zincalume® (ZIN) and EPDM (EPD) panels. Concentrations of organics in runoff from the roofing panels were low and generally not distinguishable from concentrations in runoff from the glass control panels.

Ecology found that asphalt shingle, built-up, modified-built-up, TPO without brominated flame retardant, concrete tile, and untreated wood shingle roofing materials did not release elevated levels of the metals or organic compounds evaluated in runoff. However, asphalt shingle roofing materials with algae-resistant (AR) copper granules do release copper. The copper-releasing granules used in this roofing material can help prevent algae from developing on a roof but are not effective at preventing moss formation.

Total Metals

Table ES-2 summarizes median metals concentrations in runoff from the roofing materials evaluated across all 20 rain events and highlights those that were statistically different than the glass controls. Statistical comparisons between concentrations in runoff from the roofing materials and glass controls inherently assume that concentrations in runoff from the glass controls measure atmospheric deposition or leaching from the glass. The *Conclusions* section in this report describes panel-specific runoff concentrations and differences in greater detail.

The statistical differences identified in Table ES-2 do not address whether the runoff exceeds a threshold (e.g., water quality criteria, permit limits, or benchmarks). Such comparisons would require additional understanding of the fate and transport of the metals.

Table ES-3 identifies whether the metals concentrations in runoff from the panels were significantly different between Rounds 1 and 2. For all roofing materials in which significant differences were identified, except one, Round 2 concentrations decreased, indicating weathering may have occurred. Runoff from the painted galvanized metal panel (PAZ) significantly increased in its zinc concentrations.

Correlations between Metals and Rain Event Properties

In several instances, Ecology identified statistically significant correlations between total metals concentrations and:

- Total precipitation (inverse correlations)
- Average rain intensity (inverse correlations)
- Length of the antecedent dry period (positive correlations)

These correlations are consistent with observations reported in the literature.

Table ES-2. Median metals concentrations (ug/L) in the roofing panel runoff across 20 rain events and statistical differences from controls.

Roofing Material (Identification Code)	**Estimated percent of roof area in Puget Sound basin***	**Median concentrations across all 20 rain events**				
		Arsenic	**Cadmium**	**Copper**	**Lead**	**Zinc**
Asphalt shingle with AR (AAR)	71	**0.21**	0.005	**30**	**0.05**[a]	**6.4**
Asphalt shingle without AR (AS[A])		**0.08**	0.005	**2.1**	**0.06**	**2.7**
Copper (CPR)	0.3	**0.05**	**0.015**	**1,905**	**0.22**	**4.0**
Concrete tile (CTI)	2.9	**0.35**	0.005	**0.63**	**0.32**	**4.3**
Painted galvanized steel (PAZ)	5.3	**0.07**	0.005	**0.56**	**0.18**	**52**
Zincalume® (ZIN)		**0.08**	0.005	**0.50**	**0.18**	**114**
Treated wood shake (TWO)	6.5	**1,385**	**0.105**	**825**	**0.03**[a]	**8.8**
Wood shingle (WOS)		**0.12**	0.005	**0.74**	**0.04**[a]	**5.6**
Modified built-up roof with atactic polypropylene (APP) granulated cap sheet (BUA)	13	**0.06**	0.005	**0.51**	**0.03**[a]	**2.9**
Built-up roof with oxidized asphalt granulated cap sheet (BUR)		**0.08**	0.005	**0.46**	**0.04**[a]	**2.5**
Modified built-up roof with styrene butadiene styrene (SBS) granulated cap sheet (BUS)		**0.10**	0.005	**0.37**	**0.04**[a]	**2.5**
Ethylene propylene diene terpolymer (EPD)	unknown	**0.07**	0.005	**0.38**	**0.13**	**57**
Polyvinyl chloride (PVC)		**21**	0.005	**0.43**	**0.17**	**5.1**
Thermoplastic polyolefin (TPO)		**0.06**	0.005	**0.48**	**0.12**	**3.5**
Steep-slope glass control		**0.07**	0.005	**0.40**	**0.14**	**3.7**
Low-slope glass control		**0.08**	0.005	**0.46**	**0.17**	**4.1**

* Based on Appendix B of Ecology, 2011a.

[A] Average of three replicate asphalt shingle panels (AS-1, AS-2, and AS-3).

Yellow shading indicates significantly higher concentrations than glass controls at α= 0.05.

[a] Green shading indicates significantly lower concentrations than glass controls at α= 0.05.

Bold indicates analyte detected at or above the method detection limit (MDL).

Table ES-3. Statistical differences in panel runoff concentrations between Rounds 1 and 2.

Roofing Material (Identification Code)	**Arsenic**	**Cadmium**	**Copper**	**Lead**	**Zinc**
Asphalt shingle with AR (AAR)					*
Asphalt shingle without AR (AS[A])			*		
Copper (CPR)					
Concrete tile (CTI)					
Painted galvanized steel (PAZ)					a
Zincalume® (ZIN)					
Treated wood shake (TWO)	*	*	*		*
Wood shingle (WOS)					*
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 terpolymer (EPD)					*
Polyvinyl chloride (PVC)	*				*
Thermoplastic polyolefin (TPO)					
Steep-slope glass control	*				
Low-slope glass control	*				

[A] Average of three replicate asphalt shingle panels (AS-1, AS-2, and AS-3).
***** Yellow shading indicates significantly lower concentrations in Round 2 at $\alpha = 0.05$.
[a] Green shading indicates significantly higher concentrations in Round 2 at $\alpha = 0.05$.

Total Metals Released from the Panels

Ecology calculated the total metals released to runoff only for those roofing materials with runoff that showed significant differences from the glass controls. Ecology recognized that release rates should not be broadly applied for the following reasons:

- The release rates changed with the aging of the panels, even in the short one-year period from the beginning of the study.
- The relationships between concentration and amount of precipitation, its intensity, and antecedent dry period vary. Using an average, median, or range values to calculate whole basin releases may not accurately represent the conditions within the basin.
- The panels used in this study represented a run-length of less than 3 meters, much less than on most residential or commercial roofs. Longer run-length roofs would likely release greater loads of metals than those calculated.

Comparison with Puget Sound Toxics Assessment

The concentrations of metals in runoff obtained for Round 2 were compared to concentrations used to estimate releases within the Puget Sound basin from the Puget Sound Toxics Assessment (Ecology, 2011a). Only copper concentrations in runoff from the copper panel (CPR) were similar to those used to establish releases within the Puget Sound basin. With this single exception, the comparisons revealed that concentrations used in the Puget Sound Toxics Assessment (Ecology, 2011a) ranged from 30% higher to 1,000 times higher. 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 a single component of roofing systems, namely roofing materials.

Because runoff concentrations depend on a number of factors – including the specific roofing material and components, age of the materials, length of the roof, angle of roof installation, and climatic conditions – application of literature runoff concentrations to basin-wide releases should be undertaken cautiously.

Organic Compounds

Concentrations of PAHs in runoff from the roofing panels were low and generally not distinguishable from concentrations from the glass control panels, even in those roofs which have asphalt components (such as asphalt shingle, built-up, and modified built-up roofing). Median total PAH concentrations in runoff from all but one panel appeared to increase in Round 2 over concentrations measured in Round 1.

Concentrations of phthalates in runoff from the roofing panels were low across all panels. Phthalates concentrations observed in runoff from the treated wood shake panel (TWO) in Round 1 were no longer distinguishable from concentrations from the glass control panel in Round 2 of the study.

During Round 1, PBDEs concentrations in runoff were low and not distinguishable from concentrations from the glass control panels. During Round 2, no PBDEs were detected in runoff from any of the roofing panels.

Recommendations

As roofing materials continue to age, concentrations of metals released may change over a 10-year to 30-year life of a roof. Ecology recommends continued monitoring to determine the impacts of roof aging on total metals release. Monitoring can be continued at intervals at the Washington Stormwater Center in Puyallup, Washington, where the roofing panels have been relocated.

While the roofing materials evaluated in this study do not appear to be releasing substantial concentrations of organics, these compounds 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. Greater specificity for future monitoring of both metals and organics is described in Winters and Graunke (2014).

Given that even the highest zinc concentrations in runoff from the Zincalume® (ZIN) and EPDM roofs were an order of magnitude lower than the concentrations used by Ecology to assess 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 RTF provided the following additional recommendations:

- Evaluate fate and transport of those metals that, based on their concentration and/or their abundance in the region, may impact fresh and marine waters of the Puget Sound basin, as also recommended by some members of the RTF in Windward (2014).
- Assess the potential contributions of after-market roofing treatments including illegal or non-approved roofing treatments.
- Develop educational materials for appropriate use of maintenance and moss control products.
- Monitor UV intensity as part of roof aging studies.
- Assess the effectiveness of mesocosm or bioretention columns (at the Washington Stormwater Center) in removing metals in runoff from some of the roofing panels.
- Because both scale and roofing components appear to play significant roles in releases, consider a full-scale roofing system study, particularly for roofing systems on the larger commercial buildings, such as galvanized metal, Zincalume®, and EPDM. Secondly, researchers should conduct an update of the relative usages of specific roofing types in the Puget Sound basin. Finally, researchers should pair these data sets to estimate releases from roofing systems within the Puget Sound basin.

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 could be associated with roof runoff (Ecology, 2011a and b). The reports also noted that polycyclic aromatic hydrocarbons (PAHs) and phthalates may also be released[1] from roofing systems.

The assessment used literature values from various locations across the U.S. and around the world to represent contaminant concentrations in roof runoff in the Puget Sound basin. A number of regional climatic factors such as precipitation amount, intensity, and duration; pH; and roofing materials typically used in the basin could have a significant impact on the release of contaminants from roofing materials (Winters and Graunke, 2014).

Need for a Puget Sound-Specific Study

Based on generalized conclusions from the Puget Sound Toxics Assessment (Ecology 2011a) and a subsequent literature review, Ecology wanted to gain a better understanding of region-specific information related to contaminant levels in roof runoff.

A comprehensive and controlled assessment of runoff from various roofing materials had 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. Western Washington experiences slightly acidic rain, ranging in pH from 4.95 to 5.4 (NADP, 2012). These pH values are less acidic than the 4.3 pH value measured by Clark in the most extensive study of roofing materials in the U.S. which controlled for atmospheric deposition (Clark, 2010).

Further, little evaluation has been conducted of the newer, synthetic materials such as ethylene propylene diene terpolymer (EPDM[2]), thermoplastic polyolefin (TPO), or flexible polyvinyl chloride (PVC). Because these types of roofing materials have multiple product additives, they might be expected to release metals, biocides, and phthalates into stormwater runoff. Runoff from these materials has not been assessed for many of the chemicals that could potentially leach from them. Further, researchers have not evaluated PAHs in runoff from asphalt shingle roofs, built-up roofs (BUR), and modified BURs installed using either coal tar or asphalt.

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[1] In the context of this report, *released* and *leached* are used interchangeably to mean release by leaching, dissolution, or other chemical and physical processes where the resultant concentrations are statistically discernible from the glass controls.

[2] The "M" in EPDM indicates a class of rubber having a saturated chain of the polymethylene type.

Ecology applied for and received funding from the National Estuary Program (NEP) to conduct an initial assessment of runoff from roofing in the Puget Sound basin, with collaboration from stakeholders.

Roofing Task Force Involvement

The design and implementation of the study included collaboration with 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.

To assess the roofing systems systematically within the budget available, the RTF helped Ecology focus the pilot study on obtaining information from one component of roofing systems: the roofing materials. Ecology and the RTF recognized that roofing systems are complex and include not only the roofing materials, but also gutters, downspouts, HVAC systems, flashings, exposed fasteners, and post-manufactured treatments, to name a few. Ecology and the RTF also recognized that where elevated levels of contaminants run off of roofing systems, fate and transport modeling and hazard assessments can assist in understanding potential impacts on waters of the Puget Sound basin.

The pilot study offered the first step in a systematic approach to assessing toxic chemicals in roofing systems. The study assessed roofing materials most commonly used in the region based on surveys and RTF member knowledge. Discussions with the RTF also narrowed the focus of the study to new roofing materials (i.e., un-aged materials). The RTF members selected, provided, and installed the roofing materials at the beginning of the study.

RTF members provided substantial comments on this study as well as the initial study from the first 10 rain events (Round 1) entitled *Roofing Materials Assessment: Investigation of Toxic Chemicals in Roof Runoff* (Winters and Graunke, 2014).

Purpose of Round 2 of the Study

Following completion of sampling during the first 10 rain events (Round 1), Ecology and the RTF determined that a more robust baseline was needed. An expanded baseline from a single location over a one-year period would better inform future studies of the roofing panels after they are moved to the Washington Stormwater Center in Puyallup, Washington. A strong baseline would also better serve in making comparisons with runoff from other roofing components that Ecology may research. Greater numbers of samples would also provide greater statistical power in discerning differences between roofing materials and changes over time.

Ecology determined that collection of additional rain event data would allow the agency to gain confidence in the results, prioritize further actions related to assessing roofing systems, and determine the need to evaluate other sources of contaminants in the Puget Sound basin.

Thus, Ecology sought additional funding (from NEP and ARMA[3]) to support sampling and analysis of an additional 10 rain events (Round 2) in the fall 2013 and winter 2014.

Ecology and the RTF designed Round 1 and 2 studies to provide better information to assess contaminants released to stormwater from new roofing materials in the Puget Sound basin by collecting data using:

- Specific roofing materials used in the basin.
- Runoff generated by actual climatic conditions in the Puget Sound area.
- Controls for factors such as concentrations of contaminants in atmospheric deposition.

Both Round 1 and 2 studies focused on obtaining information from one component of roofing systems: the roofing materials using only new roofing materials (i.e., materials aged over the one-year period of the two rounds of the study).

Objectives

The objectives of Round 2 of the Roofing Assessment were to determine:

- A baseline range of concentrations of specific chemicals released from selected new roofing materials used in the Puget Sound basin by analyzing runoff from these roofing materials over a one-year period.
- Whether changes occur in chemical concentrations in the runoff between the first 10 rain events (Round 1) and the second 10 rain events (Round 2), reflecting the impacts of weathering/aging.
- The concentrations of metals released (in ug/m^2) in the runoff from the roofing materials.
- Whether roofing materials release potential contaminants at different rates with different precipitation amounts, intensities, durations, or antecedent dry periods.

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. Neither this study nor the previous study (Winters and Graunke, 2014) recommends specific products for use by the roof manufacturing community, construction contractors, roofing designers, homeowners, or others.

Results of this study are intended to help guide Ecology and the RTF in making recommendations for follow-up actions and investigations. The study can also provide a better understanding of the role of roofing systems in releasing toxic chemicals within the Puget Sound basin. The *Recommendations* section of this report includes actions recommended by the RTF, as well as actions recommended by Ecology.

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[3] Asphalt Roofing Manufacturers Association

Methods and Study Design

This study evaluated a second round of stormwater runoff from 18 constructed, pilot-scale roof panels in the fall of 2013 and winter of 2014. Ecology reported the first round of sampling in *Roofing Materials Assessment: Investigation of Toxic Chemicals in Roof Runoff* (Winters and Graunke, 2014).

This section provides a general description of the roofing materials assessment and procedures that differed from those described in the Quality Assurance (QA) Project Plan (Ecology, 2013a) and its Addendum (Ecology, 2013b).

Roofing Materials

The study evaluated runoff from 18 constructed roof panels including triplicate asphalt shingle panels and two glass control panels. Table 1 lists the roofing material types by slope and the measured surface areas of each roof exposed to precipitation. All roofing panels faced south-southwest, the direction of the prevailing wind. Steep-slope roof panels were installed at a 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 1 are used in subsequent tables and figures of this report to refer to roofing materials installed on the panels. Appendix A of Winters and Graunke (2014) gives descriptions of each of the panel types and their installation. Figure 1 depicts the layout of the site.

Ecology constructed all 18 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 different types of roofing materials for the pilot study. The design included 3 replicates of the asphalt shingle roofing and 2 glass controls. 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 panels to serve as controls, one steep-slope and one low-slope.

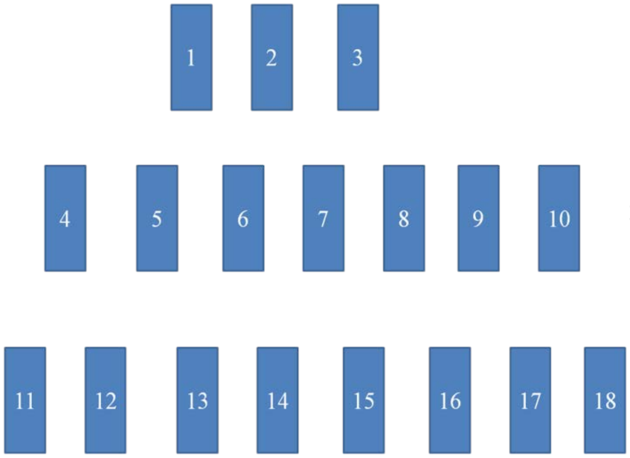
To assess variability, three replicates of the asphalt shingle without algal-resistant (AR) granules were constructed. This roofing material was selected for replication as it represents 71% of the roofing used in the Puget Sound basin (Ecology, 2011a). Asphalt shingles without AR represent the largest 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).

Table 1. 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 roofing with atactic polypropylene (APP) granulated cap sheet	33.8	3.14
BUR	Built-up roofing with oxidized asphalt granulated cap sheet	33.4	3.11
BUS	Modified built-up roofing with styrene butadiene styrene (SBS) granulated cap sheet	33.5	3.12
EPD	Ethylene propylene diene terpolymer (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.

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. Washington State Department of Ecology headquarters building is in the background. Photograph provided courtesy of Russ McMillan, Department of Ecology.

Each of the asphalt shingle panels without AR was installed using shingles donated by 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 processes. 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.

All 18 panels were exposed to the same precipitation events and the same wind direction simultaneously. Ecology recorded the precipitation with a tipping bucket rain gage that was co-located with the panels. The bucket recorded in increments of 0.01-inch of precipitation. Ecology calibrated the rain gage prior to Round 1 sampling and checked the calibration prior to initiation of Round 2 sampling.

Decontamination

Ecology staff decontaminated the panels, gutters, and sample collection equipment as described in the original QA Project Plan (Ecology, 2013a) with the minor differences detailed in Appendix B of Winters and Graunke (2014). Prior to Round 2 monitoring, Ecology decontaminated the gutters and sample collection equipment as described in Appendix B of the QA Project Plan (Ecology, 2013a).

After each rain event during Round 2, staff initially decontaminated the gutters first with rain water remaining in the stainless-steel collection containers after sampling, then with a rinse of 50 to 100 ml of distilled deionized (DI) water. This minor change did not affect the outcome of the study.

Sample Collection

Ecology collected and analyzed runoff from the panels during 10 rain events between October 30, 2013, and January 30, 2014 (Round 2 or Events 11-20) in accordance with the QA Project Plan (Ecology, 2013a) and its addendum (Ecology, 2013b). Ecology's Manchester Environmental Laboratory analyzed samples for metals (arsenic, cadmium, copper, lead, and zinc), PAHs, phthalates, and polybrominated diphenyl ethers (PBDEs).

The QA Project Plan (Ecology, 2013a) defines a qualifying rain event as greater than 0.1 inch (2.54 mm). Ecology decided to allow sampling of smaller events than described in the QA Project Plan (Ecology, 2013a) for Round 1. For seven of the rain events during Round 2, the laboratory required less sample volume because only total metals were analyzed for these events. This enabled Ecology to assess the effects of smaller rain events on concentrations.

Staff targeted rain events for sampling when the weather forecast predicted at least 0.05 mm of precipitation in a 24-hour period. Weather reports were reviewed daily to determine whether six hours had elapsed since the preceding rain event with less than 0.05 mm of precipitation and whether the rain event was predicted to be of sufficient size. 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.

Staff could terminate collection of a rain event for one of three reasons:

- Ecology did not want to allow the sample collection containers to overflow. If sample volume approached the maximum collection-container volume (63.1 liters), staff recorded the time and quickly removed the gutters from the apparatus, ceasing runoff collection.
- For some events, sample collection was terminated to maintain the defined 24-hour limit of a rain event.
- Ecology terminated collection (by removing the gutters) to control the size of a sampled event. During Round 1, rain events ranged between the 52nd and 91st percentiles of precipitation falling within a 24-hour period for this location. Ecology was interested in expanding that distribution on the lower end during Round 2 to broaden the applicability of the data.

Runoff in each of the stainless-steel containers was measured for depth and tested for pH, temperature, and specific conductance using calibrated meters. Appendix A provides the field notes with the pH, temperature, and conductance values recorded.

For the lower precipitation rain events, the volume collected in the stainless-steel containers was small and prohibited the use of the churn-splitter type mixing device used in the higher precipitation events. Instead, samples were dipped out of the stainless-steel container with a decontaminated stainless-steel pitcher after the volume in the container was mixed. Ecology accomplished the mixing by agitating the buckets back and forth vigorously. Swirling was not used as that caused a vortex to form in the containers. The pitcher was also used to mix the sample by filling it and releasing aliquots back into the pitcher. Ecology used this mixing technique on rain events 11, 13, 16 through 18, and 20. On the remainder of the events, Ecology used the churn-splitter mixing device as described in Appendix C of the QA Project Plan (Ecology 2013a).

Table 2 lists the types and numbers of analyses conducted and the analytical methods used for each round of sampling. For rain event 17, the project lead did not properly align the gutter beneath the asphalt shingle panel with AR (AAR). Thus, stormwater from the panel did not flow into the stainless-steel collection container, and no sample could be collected from this panel. Staff collected samples for the remaining nine events from this panel. During Round 1, samples of PAHs and phthalates were lost for the modified built-up roofing with APP (BUA).

Table 2. Number of samples analyzed and analytical methods by panel and round.

Method	**Steep-Slope Panels**								**Low-Slope Panels**							
	AAR	**AS[A]**	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**	**GST**	**BUA**	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
Round 1																
Tot. Metals EPA 200.8	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Diss. Metals EPA 200.8	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
PAHs & Phthalates EPA 8270 SIM	10	10	3	3	3	3	3	10	9	10	10	10	10	10	3	10
PBDEs EPA 8270D	3	3	3	3	3	3	3	10	10	10	10	10	10	10	3	10
Round 2																
Total Metals EPA 200.8	9	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
PAHs & Phthalates EPA 8270 SIM	2	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
PBDEs EPA 8270D	2	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3

Panel identification codes are defined in Table 1 on page 25.

Sample Management

Ecology staff preserved, labeled, and stored samples in coolers with ice. Ecology stored the coolers in a walk-in refrigerator while awaiting transport to Manchester Environmental Laboratory (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 B).

MEL provided results in Portable Document Format (PDF) (Appendix C) and in electronic format (Appendix D).

Laboratory Analysis and Data Quality

The QA Project Plan Addendum (Ecology, 2013b), in conjunction with the QA Project Plan (Ecology, 2013a), outlines the quality control and quality assurance process for this roofing assessment.

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 summarize 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. None of the deviations from the QA Project Plan adversely affected the usability of the data.

Field Quality Control Samples

For three rain events (Events 12, 15, and 17), the laboratory analyzed runoff samples from all panels for total metals (arsenic, cadmium, copper, lead, and zinc), PAHs, phthalates, and PBDEs. All other rain events were analyzed for total metals in accordance with the QA Project Plan Addendum (Ecology, 2013a). Table 2 lists the analytical methods used

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

For the remaining panels, staff obtained field split samples at locations listed in Table 3. Field splits served 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.

Staff obtained matrix spike (MS) samples and matrix spike duplicates (MSD) at two of the same locations as the field splits (Table 3). Equipment rinse blanks were obtained for each rain event as described in Appendix B of Winters and Graunke (2014).

Table 3. Schedule of field split and matrix spike/matrix spike duplicate samples taken by rain event.

Rain Event	Rain Event Date	MS/MSDs and Splits	Splits Only
Round 1			
1	22-Feb-13	CPR, AS-1, BUA[1]	
2	25-Feb-13	PAZ, GST, EPD	
3	28-Feb-13	TWO, AAR, TPO	
4	6-Mar-13	EPD, GST, GLO	
5	12-Mar-13	GST, TPO, PVC	
6	13-Mar-13	EPD, GLO, DIW	
7	20-Mar-13	AS-2, BUR, WOS[2], PVC[4]	
8	5-Apr-13	AS-3[5], BUS[5], ERW	
9	11-Apr-13	CTI[2], AAR[5], CPR[2], AS-2[3], BUA[3] GLO[4]	
10	19-Apr-13	PAZ[2], TWO[2], BUR[3], TPO[3], PVC	
Round 2			
11	31-Oct-13	AAR, TWO	GST
12	7-Nov-13	CPR, EPD	TPO
13	15-Nov-13	AS-1, ZIN	AS-3
14	1-Dec-13	WOS, BUS	BUA
15	13-Dec-13	CTI, GLO	PAZ
16	23-Dec-14	BUR, AS-2	AS-1
17	2-Jan-14	TWO, PVC	CTI
18	7-Jan-14	BUA, PAZ	BUR
19	1-Jan-14	AS-3, TPO	PVC
20	28-Jan-14	CPR, GST	AS-2

DIW: Distilled, deionized water blank
ERW: Equipment rinse blank
[1] Error in labeling; no MS/MSD samples were analyzed on this sample.
[2] Metals only
[3] PAHs and phthalates only
[4] PBDEs only
[5] Metals and PAHs/phthalates only
Panel identification codes are defined in Table 1 on page 25.

Laboratory Quality Control

Manchester Environmental Laboratory (MEL) conducted the laboratory analysis and laboratory QC. MEL also provided data QA in the form of narrative reports. Appendix C provides the narrative reports. Generally, MEL met the data quality objectives and measurement quality objectives described in the QA Project Plan (Ecology, 2013a) and its addendum (Ecology, 2013b), with the minor exceptions described in Appendix B of Winters and Graunke (2014).

These exceptions did not result in a completeness of less than the 90% prescribed in the QA Project Plan. MEL qualified the data they delivered.

Data Qualifiers

Ecology's technical lead conducted overall project QA. As qualified, all laboratory data were determined usable 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 D. Staff applied additional detailed flags in the final two columns of the Excel spreadsheets in Appendix D—either individual flags or a combination of flags, depending on the reasons for qualifiers. The more detailed qualifiers give a better understanding of the data and are listed only in the electronic data deliverables (EDDs) (Appendix D).

Generally, for rain events 11 through 20, data flags, other than only either J (analyte detected between the method detection limit [MDL] and the reporting limit [RL]) or U (analyte not detected at the MDL) in the EDDs in Appendix D, ranged between 2% and 36%, averaging 17% for metals. The vast majority of these flags resulted from equipment rinse contamination. Similarly, data flags for organics (other than J or U flags) ranged from 1% to 8% of the PAH and phthalate analytical results, except for flags due to method blank contamination. Method blank contamination for phthalates resulted in 46% to 66% of the results receiving a qualifier and an elevated detection limit. Laboratory contamination is discussed further in the subsequent subsection.

For the data tables in the body of this report and in Appendix B, the more conventional 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 whose 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. Organics results with concentrations less than or equal to five times those reported for the method blank (laboratory contaminant threshold) were qualified as undetected.

PAHs and phthalates were analyzed using EPA method 8270SIM in both Rounds 1 and 2. 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 among background contamination ("noise"), the capability of the instrumentation, and actual analytes released from roofing materials is difficult at these low concentrations. For future evaluation, selection of appropriate methods for organic contaminant analysis should be based on project-specific goals.

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, as well as metals associated with the stainless-steel sampling containers, the mixing devices, or tubing.

DI water blanks included trace concentrations of one or more of the metals, with an average of two metal detections per sampling event. Copper and zinc were the most common low-level contaminants in the DI water blank. Copper was detected in 100% of the DI water blanks. Copper concentrations in the DI water blanks represented between 13% and over 100% of the concentrations measured in the equipment rinse blanks. Zinc concentrations were found in five of the 10 DI water blanks, ranging from 87% to greater than 100% of the concentrations found in the equipment rinse blanks. Four of the DI water blanks exceeded 100% of the concentration found in the equipment rinse blanks. DI water blank results did not have direct implications for the runoff results. Thus, these results were not used to qualify the sample data.

The DI water came from the laboratory in one-gallon glass jars. DI water was used for the equipment rinse blanks, equipment decontamination between sampling events, and gutter rinsing. The DI water that was used for the equipment rinse blank samples did not necessarily originate from the same jar as the DI water blank.

Given that the DI water contributed a portion of contaminants measured in the equipment rinse, detections in the equipment rinse blanks were thought to reflect more than the contaminants contributed by the equipment. Metals in the runoff samples with concentrations less than or equal to five times the equipment rinse were qualified as estimated (J-flagged) rather than non-detected. This same procedure was followed for detections in the method blanks. Method blank contamination qualified only 5.8% of the runoff data across both rounds. Appendix D includes specific data qualifiers that differentiate between equipment rinse blanks and method blank contaminants.

Ecology calculated the average of split samples or field replicate samples for use in subsequent summary statistics. Where the laboratory reported a detected metal in one of these samples but not in the replicate or split sample, staff calculated the average by substituting one-half of the concentration of the MDL for the undetected value. This approach differs from a common approach to substitute either the RL or the MDL for the undetected value. Substitution of either of those two values would lead to an overestimate of the total metals present.

Helsel (2005) indicates that any substitution can induce a detection not present in the original data or obscure one that is present. However, in this case, 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 in the split sample. Use of one-half of the MDL may artificially inflate the total calculation but less than use of either the MDL or RL. Use of either the RL or the MDL for these calculations would not improve the ability to differentiate among runoff concentrations from the different roofing panels.

Helsel (2005) also indicates that standard nonparametric tests, such as rank sum tests used in this report, can be calculated by assigning the non-detected values a value below the detection limit and less that the lowest observation. “The ranks will efficiently capture the information in the data including the proportion of nondetects, accurately representing what is known about the data. Test results are reliable, not based on ‘information’ that is not known, and not dependant on the substitution of arbitrary values.” (Helsel, 2005).

On that basis, for metals reported as non-detected (U- flagged) by the laboratory, one-half of the MDL was used for calculating medians and making other statistical comparisons. This methodology follows the same procedure undertaken with the Round 1 data (Winters and Graunke, 2014).

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, rainfall intensity, season, amount of aerial deposition that accumulates between storms, land uses, and sampling bias towards first-flush or not, to name a few.

Ecology reduced sampling variability by collecting 100% of the precipitation that ran off a roofing panel from a specific size event, rather than from only the first flush, and obtained the equivalent to an event mean concentration. Sub-sampling variability was minimized by mixing before removing aliquots into sample containers. Ecology assessed sampling variability using field splits. However, field split variability also includes analytical variability. Thus, despite the design scheme to reduce variability, Ecology observed variability of concentrations in the panel runoff samples between split and replicate 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. RSD ranges, medians, and means are presented by analyte in Appendix E.

Ecology calculated RSDs for the replicates from the three asphalt shingle roofs to ensure that the panels served their intended purpose as replicates. Where the average RSD for a parameter exceeded 20%, substantially lower medians indicated the presence of a few outlier values. The maximum variabilities among replicate samples (maximum RSD values) were generally observed at the lowest concentrations (Table E-1 in Appendix E). Where reported values are generally less than five times the reporting limit (RL), Mathieu (2006) determined that RSDs are higher than generally established for ambient monitoring. This was the case for outlier metals and PAH RSDs.

For the organic compounds, the RSDs of samples from the three replicate asphalt shingle panels were generally lower in Round 2 data than in Round 1 data. These met the QA Project Plan prescribed goal of 40% for the organic compounds, except for anthracene. For two rain events, anthracene was detected in one of the three replicates at two to three times the RL. When the undetected values were included in the average at half the MDL, the RSD may have been artificially inflated. As pointed out by Mathieu (2006), the low levels generally found in the ambient environment can lead to higher 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. Variability in the replicates also reflects potential variations in the shingles installed on each panel (although each of the six manufacturer's shingles placed on all three replicates was from a single lot). Ecology's sampling protocols minimized these potentially confounding factors. Thus the RSDs of the replicates would be expected to have higher RSDs than the split samples, as observed in this study.

The average RSDs for the split samples generally met the goals for metals (Table E-2 in Appendix E). When the concentrations were low, the same pattern of higher RSDs emerges. Again, where the average RSDs were higher than the goal, the median RSDs were lower, indicating a skew to the data with outliers. For organic compounds, the RSDs for the split samples were consistently lower than the goal and lower than during Round 1.

For the lower precipitation rain events, the stainless-steel containers were agitated vigorously and samples were dipped using a stainless-steel pitcher as described in the *Methods* section. Ecology used this dipping technique to mix the runoff in rain event numbers 11, 13, 16 though 18, and 20. Ecology assessed differences between the agitation/dipping and the original churn-splitter type techniques by evaluating the RSDs for the metals from the split samples (Table E-3 in Appendix E). Ecology used the split samples for this analysis because of the greater number of them than the replicate samples.

For metals, the RSDs for split samples using the dipping technique ranged from 6% to 28%, averaging 15% across the five metals. The RSDs for split metals analyses using the original churn-splitter device ranged from 10% to 23%, averaging 18% across the five metals. This would indicate that the agitation/dipping technique used for sampling low precipitation events did not introduce additional variability into the samples.

Summing Organic Constituents

Concentrations of PAHs and phthalates were generally low and spatially heterogeneous. The laboratory did not detect any polybrominated diphenyl ethers (PBDE) congeners during Round 2. 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 and phthalates) for each panel type and each rain event. Staff calculated the sums by adding concentrations that were either qualified[4] (J flagged) as estimates (i.e., values between the RL and MDL) plus those that were reported above the RL. This methodology follows the guidance provided by Era-Miller and Seiders (2008) and is the same as undertaken with Round 1 data (Winters and Graunke, 2014).

Where the laboratory reported a detected compound in one sample but not in the replicate or split sample, staff calculated the average by substituting one-half of the concentration of the MDL for the undetected value. This approach differs from a common approach to substitute either the RL or the MDL for the undetected value. Substitution of either of those two values would lead to an overestimate of the total PAHs.

Helsel (2005) indicates that any substitution can induce a detection not present in the original data or obscure one that is present. However, in this case, since the compound was detected in one of the split samples at or above the MDL, it is likely to have been present (but at a concentration less than the MDL) in the other split sample. Use of one-half of the MDL may artificially inflate the total calculation, but less than use of either the MDL or RL. Use of either the RL or the MDL for these calculations would not improve the ability to differentiate among runoff concentrations from the different roofing panels.

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[4] 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.

Results

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

Throughout this and subsequent sections of the report, roofing panels are referred to by their abbreviations as provided in Table 1. 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 slope category.

Rain Events

Table 4 shows the range of rain event data including precipitation amount, duration, peak, average, and effective intensities, as well as length of the antecedent dry period. Tables in Appendix B provide the weather-related data for each rain event in metric units from both rounds of sampling. Rain data were obtained from the tipping bucket rain gage co-located with the roofing panels.

The sampled rain event durations were calculated from the start of the rain until the gutters were removed or the rain stopped, whichever was shorter. For all events in Round 2, the collection containers and gutters were placed prior to the beginning of the event. Table 4 gives the range of antecedent rain conditions. For four rain events (12, 14, 16, and 20), the gutters were pulled to stop the sampled rain event. Staff removed gutters to terminate a rain event for three rain events during Round 1. For the remainder of the storms, there was at least a one-half hour lull in the rain event after the gutters were removed.

The sampled rain events represented a range of precipitation amounts throughout both sample rounds, as depicted in Figure 2. Figure 3 shows the distribution of the sampled rain events by rainfall amount for both rounds of sampling.

The average rain intensities (rain depth divided by rain event duration) ranged from 0.28 to 1.23 mm/hr during Round 2 (Table 4). Because some rain events included one or more 15-minute intervals without measurable amounts of rain, an effective intensity was calculated. Ecology calculated the effective intensity for those intervals when at least 0.25 mm of rain fell; these ranged from 1.27 to 2.41 mm/hr in Round 2. These values 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).

Table 4. Ranges of rain event data for sampling Rounds 1 and 2.

Metric	Round 1 Ranges	Round 2 Ranges
Rain event date(s)	2/21 – 4/19/2013	10/30/2013 – 1/28/2014
Sampled rain event duration (hrs.) [a]	2.75 – 23.25	2.42 – 23.25
Precipitation in 6 hours preceding rain event (mm)[b]	0.0 – 2.3	0.0
Hours preceding event with no measurable precipitation	0.0 – 31.5	12.75 – 141.25
Total precipitation (mm)[b]	4.31 – 18.8	1.27 – 19.30
Average rain intensity (mm/hr.)[b]	0.28 – 3.7	0.28 – 1.23
Effective intensity (Average rain intensity when rain falling) (mm/hr.)[b]	1.17 – 3.7	1.27 – 2.41
Peak rain intensity (mm/15 min.)[b]	0.51 – 1.50	0.51 – 4.57
Minimum rain intensity (mm/15 min.)[b]	0.0 – 0.25	0.0
Average temperature (°C)[c]	4.6 – 11.4	3.8 – 9.8
Low temperature (°C)[c]	2.0 – 10.6	0.0 – 8.9
High temperature (°C)[c]	6.0 – 13.3	5.0 – 11.7

a Duration = (rain event stop time and date) - (rain event start time and date).

b Data from tipping bucket rain gage co-located with roofing panels at the Department of Ecology, Lacey, WA.

c Temperature data from Olympia Airport (MesoWest http://mesowest.utah.edu/cgi-bin/droman/mesomap.cgi?state=WA&rawsflag=3).

Wind direction and speed were no longer available from KWALACEY6, the private weather station in Lacey, Washington. The nearest weather station consistently recording wind speed is the Olympia Airport, which is more than 10 miles away from the sampling site. The distance is great enough that the wind records were not deemed applicable to the site conditions; thus, no wind data were accessed for Round 2 sampling. The wind data for Round 1 are provided in Winters and Graunke (2014).

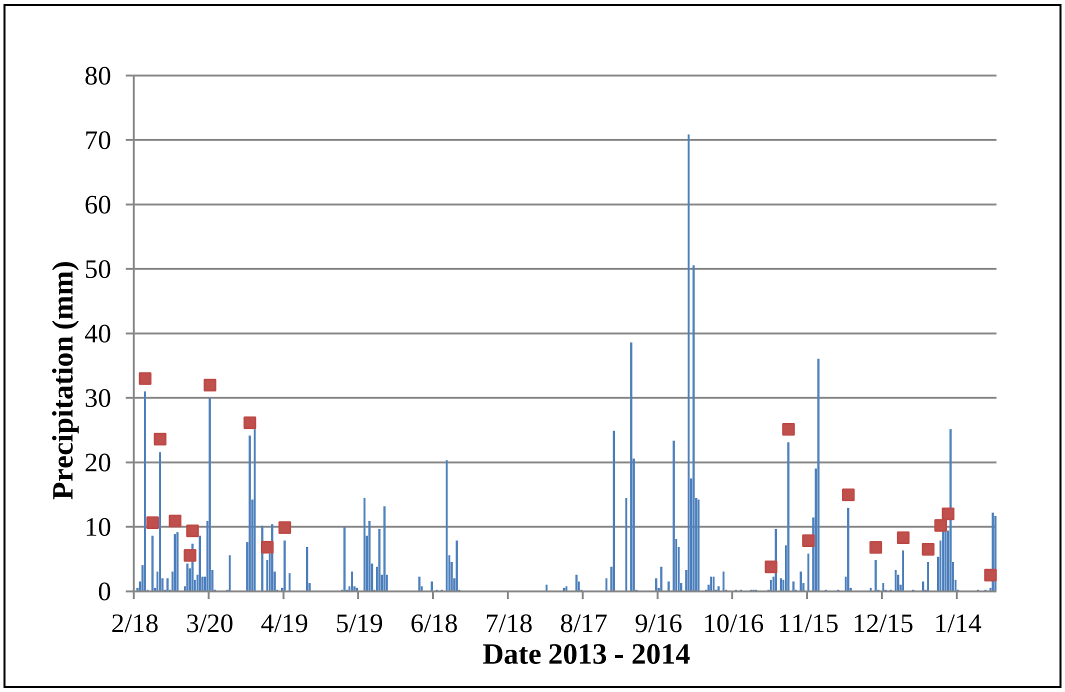

Figure 2. Hyetograph of precipitation over both sampling seasons with sample dates marked (red squares).

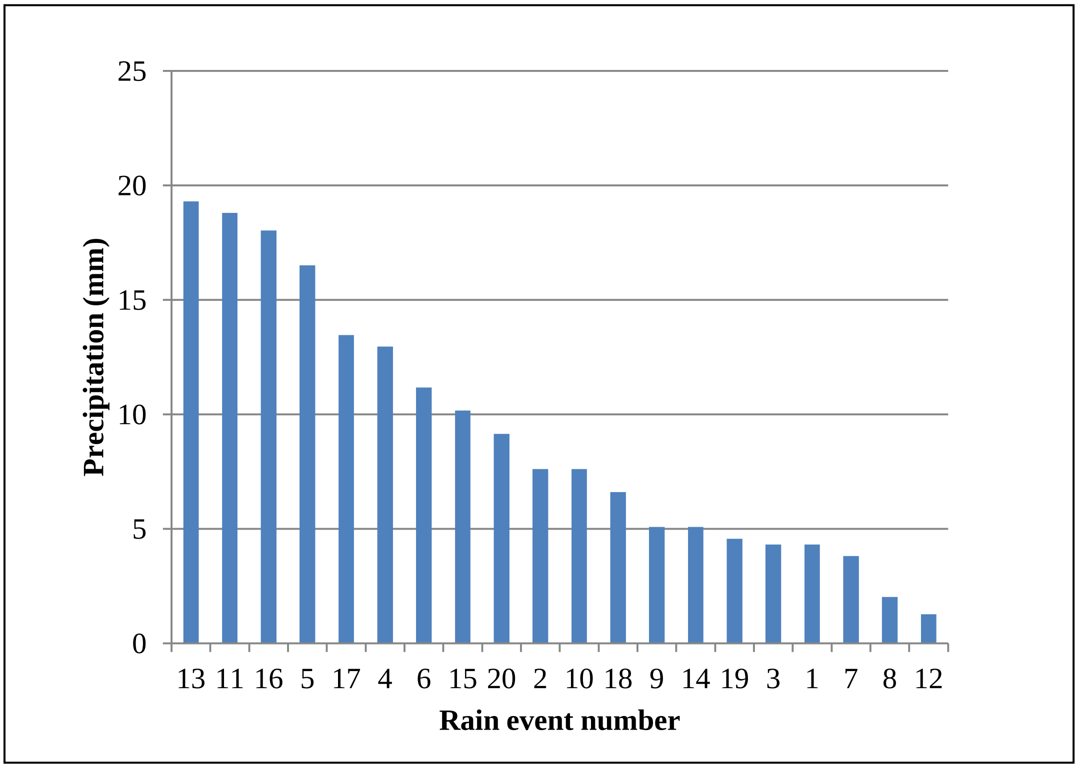

Figure 3. Distribution of rainfall amounts for sampled events (by rain event number).

Average minimum and maximum temperature data were obtained from the Olympia Airport. Ambient temperatures gradually increased with sampling dates approaching spring.

The nearest station measuring concentrations of sulfur dioxide was the Seattle Beacon Hill station. During the course of Round 2 of the study, no trace concentrations of sulfur dioxide were recorded (Puget Sound Clean Air Agency, 2013). Elevated concentrations which might result in greater release of pH-sensitive constituents such as metals were not observed.

Field Data

Table 5 shows summary statistics for pH, temperature, and specific conductance across rain events. The pH values for the glass control panels do not necessarily reflect the pH of the rain because pH varies with holding time[5]. Both pH and specific conductance reflect the composition of the roofing materials, duration of the event, as well as initial composition of the rain itself. The *Discussion* section in this report statistically compares the pH and specific conductance values in runoff from the roofing panels.

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 measured during rain event 14.

Appendix B 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 the length of time from the end of a rain event until the sample was collected and measurements were taken.

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[5] Holding time includes the length of the event and the length of time until the runoff from each panel was sampled.

Table 5. Summary of field parameters by roofing type for Rounds 1 and 2.

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**
Round 1																
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
pH 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
pH 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 Median (°C)	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
Temperature Minimum (°C)	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
Temperature Maximum (°C)	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
Spec. Cond. Median (us/cm)	11	11	4	62	5	12	80	2	4	9	8	9	3	3	3	1
Spec. Cond. Minimum (us/cm)	3	3	0	18	0	2	32	0	0	1	0	1	0	0	0	0
Spec. Cond. Maximum (us/cm)	21	26	11	116	16	24	175	10	11	25	16	25	16	13	41	17
Round 2																
pH[a] Median	6.7	7.2	6.2	7.3	5.8	4.6	3.9	4.8	5.9	6.7	6.3	5.0	4.8	5.3	5.4	5.4
pH Minimum	6.5	6.9	5.7	6.9	4.6	4.3	3.7	4.7	5.3	6.3	5.9	4.6	4.5	4.8	4.2	4.7
pH Maximum	7.1	7.3	6.9	7.6	6.5	4.8	4.2	5.7	6.5	7.5	6.7	6.2	5.3	6.0	6.0	6.4
Temperature Median (°C)	3.6	3	3	3.1	2.8	2.9	3.2	4.1	3.3	2.8	2.2	3.7	3.1	2.8	3.6	3.1
Temperature Minimum (°C)	1	1.1	0.9	1.1	0.5	0.9	1.3	0.9	1.1	0.5	0.7	1.0	0.6	0.6	1.5	0.8
Temperature Maximum (°C)	7.5	8.2	8.6	8.2	8.4	8.5	8.8	8.9	7.9	7.9	7.9	8.7	9.1	8.5	8.5	8.4
Spec. Cond. Median (us/cm)	13	17	2	63	0	12	54	0	2	14	0	1	2	2	1	0
Spec. Cond. Minimum (us/cm)	8	10	0	39	0	2	26	0	0	3	0	0	0	0	0	0
Spec. Cond. Maximum (us/cm)	43	48	32	128	18	27	95	21	16	46	17	20	16	21	19	18

[a] Rain event 9 pH data not included in median due to pH meter drift.
Shading indicates glass control panels.
Panel identification codes are defined in Table 1 on page 25.

Ecology measured the depth of runoff recovered in each stainless-steel container for each rain event and calculated the volume recovered for each roofing panel. The ranges of collected volumes are provided in Table 6. The volumes measured per rain event for each panel are provided in Appendix B.

Table 6. Summary statistics of volume of runoff collected for all 20 rain events.

Rain Event #	Total Precipitation (mm)	Volume Collected (liters)		
		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	18.8	43.7	56.9	59.6
9	10.16	25.3	27.8	29.8
10	7.61	18.9	22.8	25.8
11	2.03	4.5	7.0	7.9
12	19.3	30.8	50.7	56.1
13	1.27	4.0	5.2	6.0
14	11.18	28.8	37.7	38.7
15	5.08	12.9	16.1	17.9
16	3.81	9.4	12.9	13.9
17	4.32	5.0	12.9	12.9
18	9.14	20.9	23.6	26.8
19	12.95	33.8	45.4	46.7
20	6.6	11.9	15.2	17.4

* Measurement likely in error as volume exceeded container capacity.

Total Metals

Total metals concentrations were analyzed for every sampled rain event. Appendix B presents the concentrations of total arsenic, cadmium, copper, lead, and zinc by rain event and panel type. To assist the reader, this report presents data from both rounds of sampling. Round 1 includes rain events 1 through 10, and Round 2 includes rain events 11 through 20.

Figures 4 through 8 graphically depict the concentrations 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 1 and throughout the report. A blue vertical bar depicts samples for which no metal was detected at or above the MDL (flagged as “U” in the data tables). The blue vertical line represents a concentration of one-half the MDL. 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 three useful purposes:

- 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 multiple events in which no cadmium was detected. 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 83% and 98%, respectively.

- One can easily compare runoff quality from the steep-slope glass control (GST) on the top row (right) with other steep-sloped panels and compare the low-slope glass control (GLO) on the bottom row (right) with those of the other low-slope panels to get a visual understanding of differences in runoff concentrations.

- One can identify the possible effects of roofing material aging on concentrations of metals to runoff from the panels between the two seasons (rounds) to identify areas of potential statistical comparisons. Total metals will be discussed in greater detail in the *Discussion* section of this report.

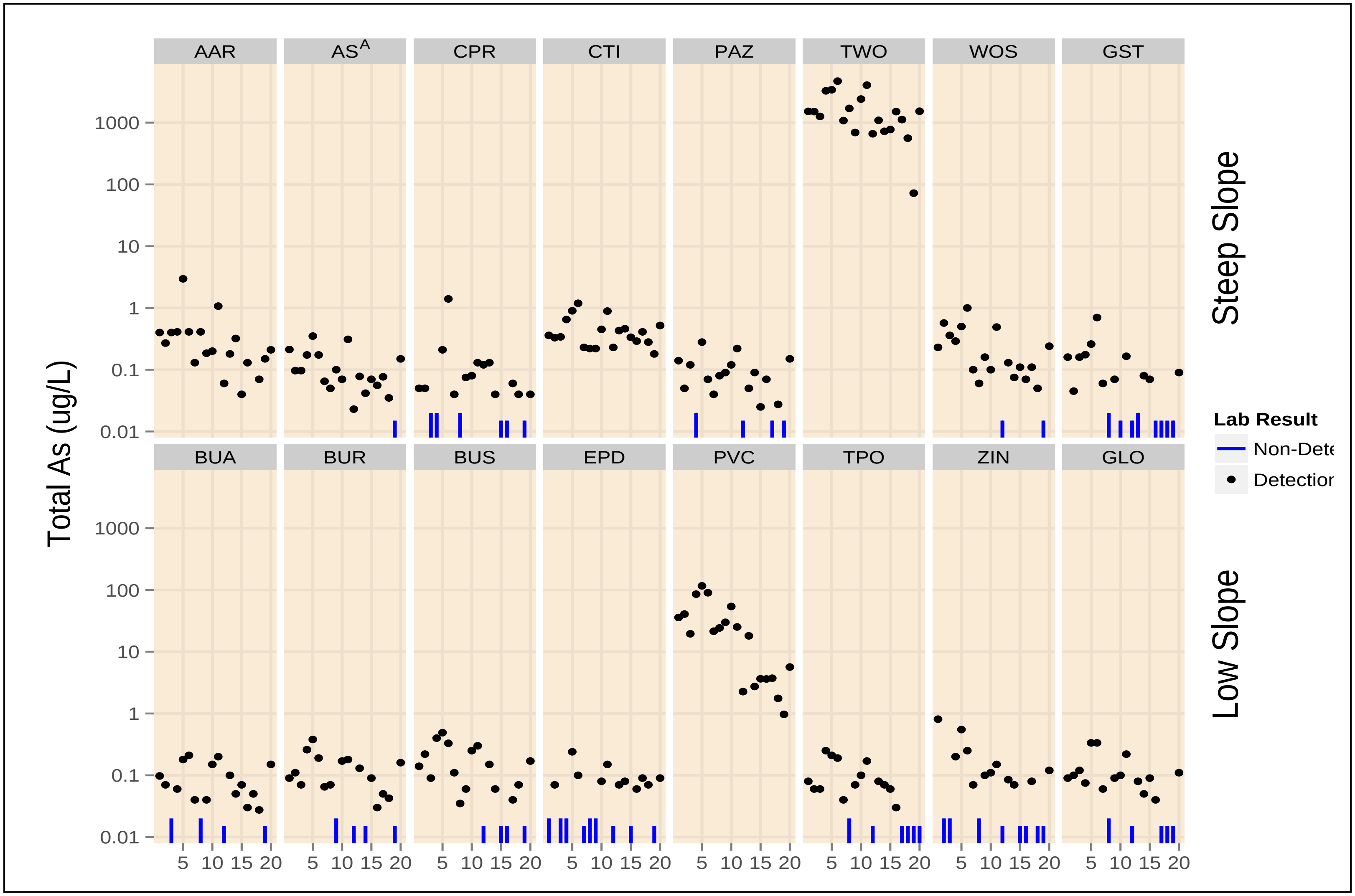

Figure 4. Total arsenic concentrations in runoff by panel and rain event number.
Panel identification codes across the top and mid-y axis are defined in Table 1 on page 25.

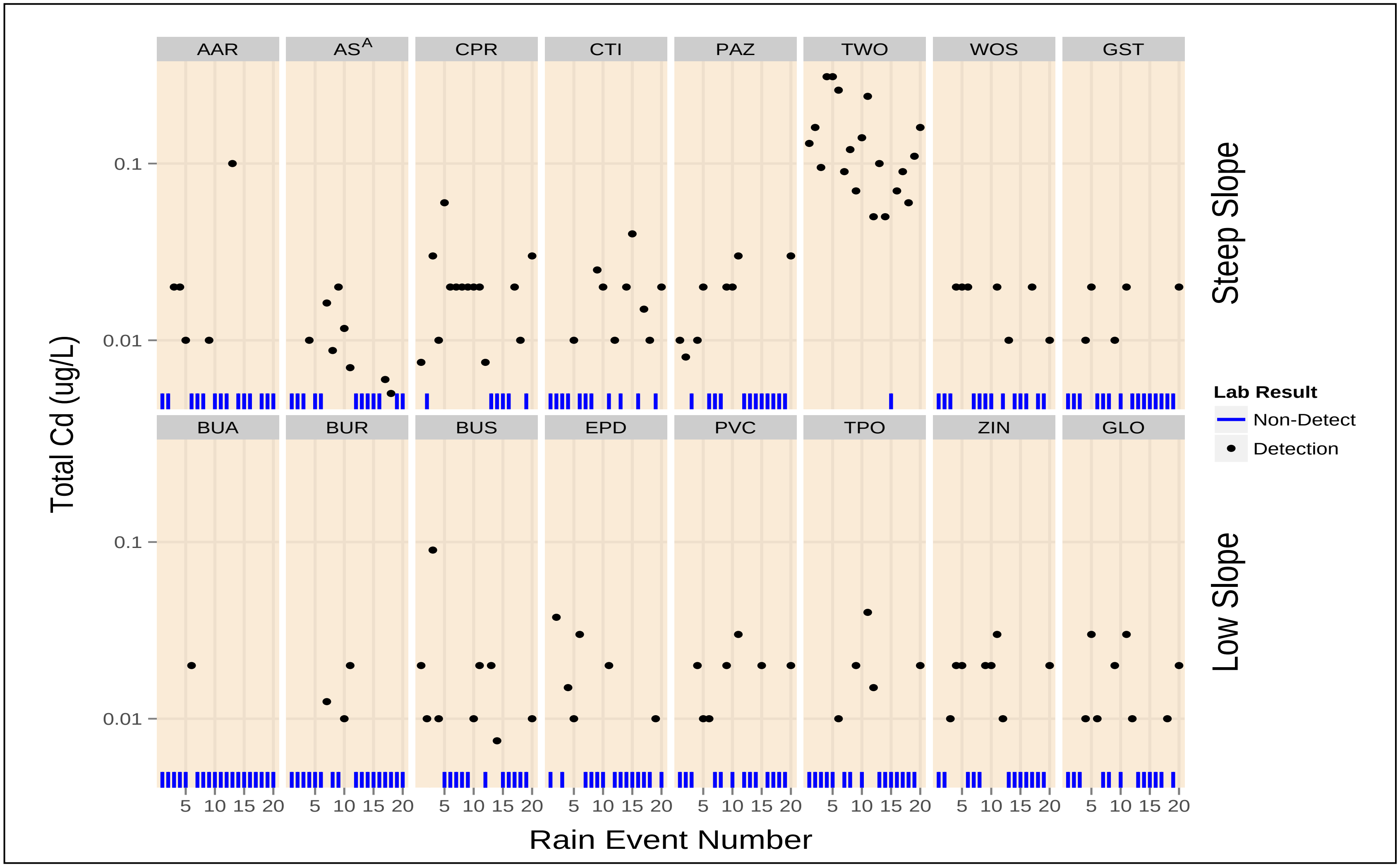

Figure 5. Total cadmium concentrations in runoff by panel and rain event number. Panel identification codes across the top and mid-y axis are defined in Table 1 on page 25.

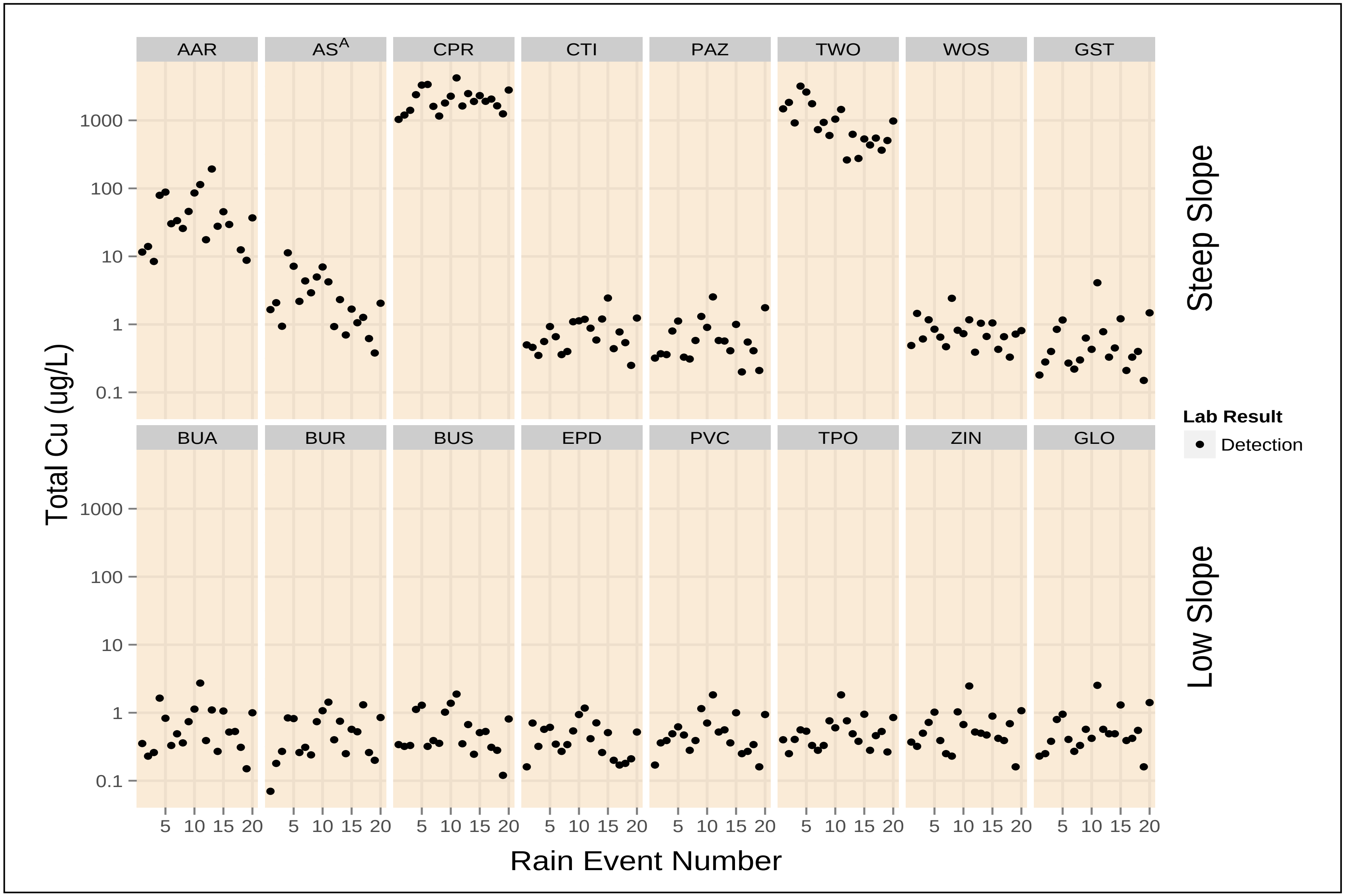

Figure 6. Total copper concentrations in runoff by panel and rain event number.

Panel identification codes across the top and mid-y axis are defined in Table 1 on page 25.

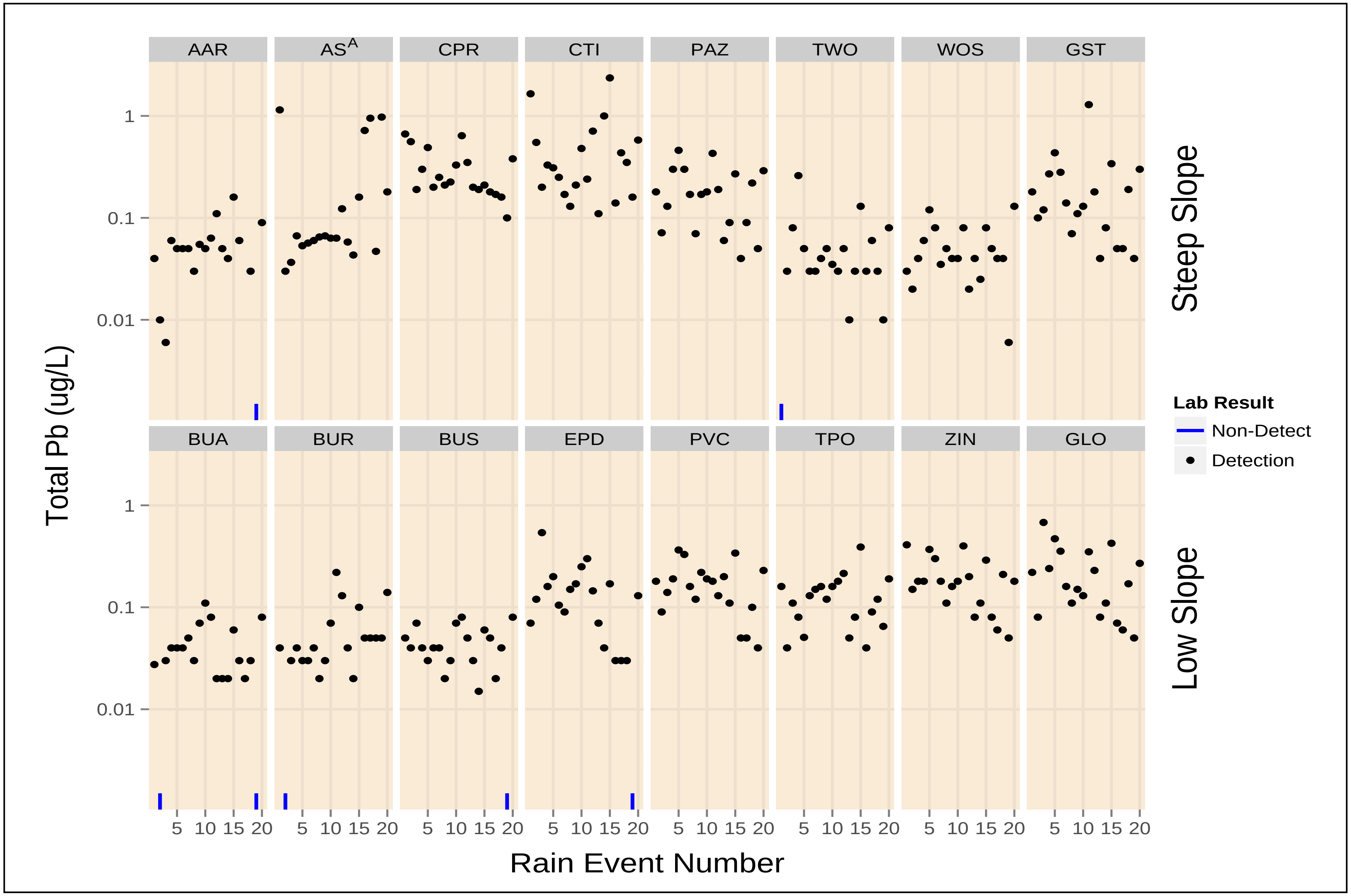

Figure 7. Total lead concentrations in runoff by panel and rain event number.
Panel identification codes across the top and mid-y axis are defined in Table 1 on page 25.

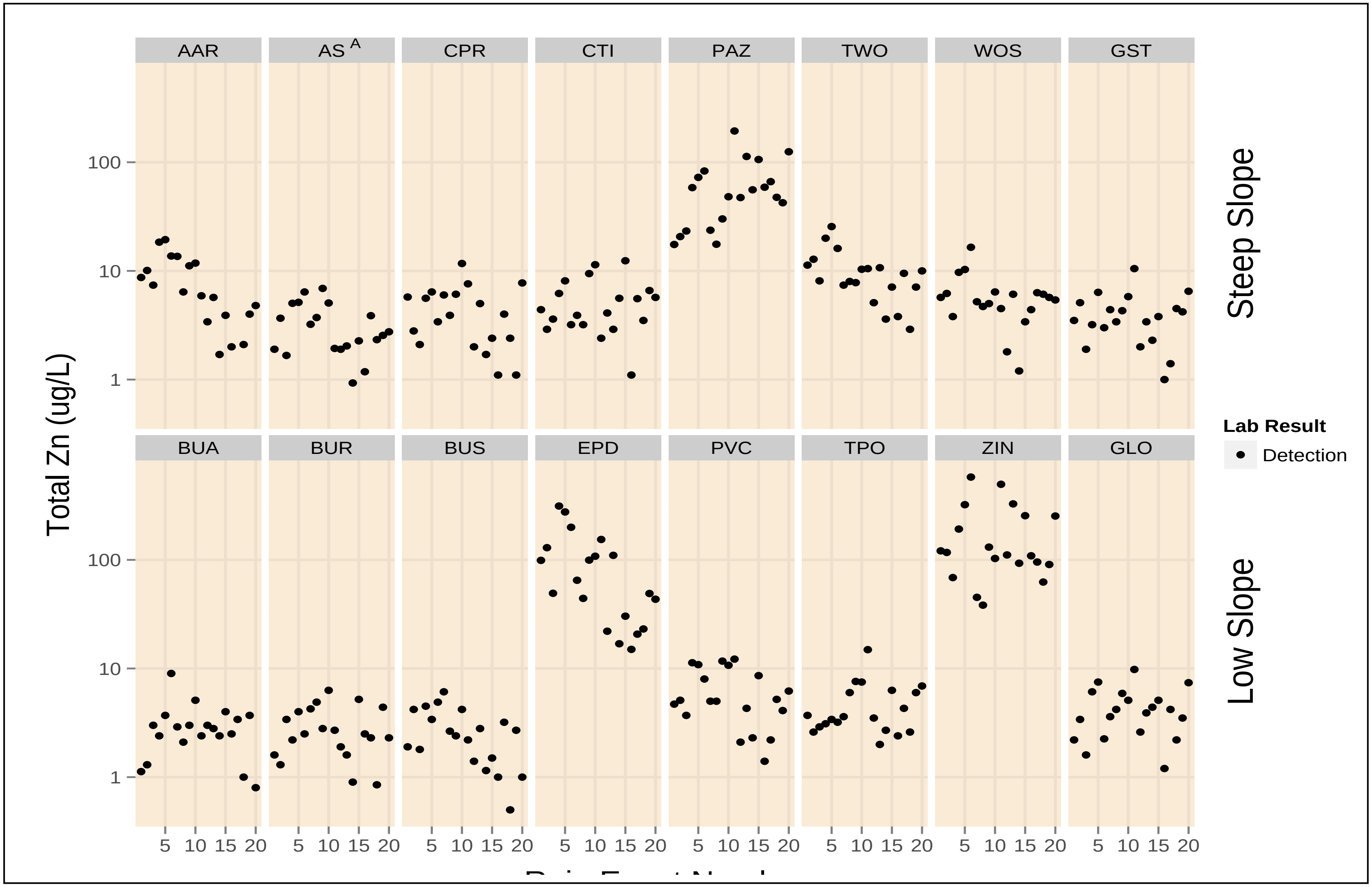

Figure 8. Total zinc concentrations in runoff by panel and rain event number.

Panel identification codes across the top and mid-y axis are defined in Table 1 on page 25.

Organic Compounds

PAHs

Ecology sampled runoff from all roofing panels for PAHs during the first three rain events in Round 1. Thereafter, staff sampled for PAHs on asphalt-based (AAR, AS^A, BUA, BUR, and BUS), single-ply, and the glass control panels. During Round 2, Ecology sampled PAHs in runoff from all roofs during three rain events (12, 15, and 17).

The numbers in Table 7 represent the percentage of sampling events in which the compound was detected in runoff from a particular panel. (Appendix B provides data tables.) Table 7 also lists the number of rain events in which PAHs were analyzed for Rounds 1 and 2. The number before the comma represents the percentage for Round 1, and the number after the comma represents the percentage for Round 2. Only those PAHs that were detected above a concentration five times the contamination in the method or equipment rinse blanks are depicted in the table. A concentration five times the concentration found in the method blank is defined as the laboratory contaminant threshold, while a concentration five times the contamination found in the equipment rinse blank is defined as the equipment blank contaminant threshold (Winters and Graunke, 2014).

All panels had PAH compounds detected in runoff in both rounds of sampling. In Round 1, phenanthrene was detected most frequently in runoff from the roof panels, while naphthalene and pyrene had less than one-half of the number of detections of phenanthrene. In Round 2, naphthalene was detected most frequently, with phenanthrene and pyrene detected slightly less frequently. Four of the 18 monitored PAHs [acenaphthene, acenaphthylene, benz(a) anthracene, and dibenzo(a,h) anthracene] were not detected in runoff from any panel in Round 1, while in Round 2 only one compound (acenaphthene) was not detected in runoff from any panel.

Ecology compared the number of times a PAH compound was detected during the first three rain events in Round 1 to the three rain events in Round 2. (Ecology determined that this type of comparison was comparable because runoff from all the panels was analyzed for organics in these events.) The numbers of compounds detected in Round 1 differed from those in Round 2. Only 191 PAH compounds were detected in Round 1, representing 22% of all possible detections, while 319 compounds were detected in Round 2, representing 38% of all possible detections.

Similar types of PAH compounds were generally detected in runoff from the steep-slope and low-slope panels with similar numbers of detections across panel types. However, the treated wood shake (TWO) and wood shingle (WOS) panels had the lowest number of PAH compounds detected in runoff during both rounds. The modified built-up roofing with the SBS cap sheet (BUS) and EPDM (EPD) panels had the greatest number of detections across rain events 1-10 (Round 1). The asphalt shingle (AS^A), copper (CPR), and concrete tile (CTI) panels had similar and high frequencies of PAH detections in Round 2, followed closely by the modified built-up roofing with the SBS cap sheet (BUS). The BUS panel had multiple detections of 1- and 2-

Table 7. Percentage of sampling events in which a PAH was detected for both sampling rounds.*

	Steep-Slope Panels								Low-Slope Panels							
	AAR	AS^A	CPR	CTI	PAZ	TWO	WOS	GST	BUA	BUR	BUS	EPD	PVC	TPO	ZIN	GLO
# Events sampled in Round 1	10	10	3	3	3	3	3	10	9	10	10	10	10	10	3	10
# Events sampled in Round 2	2	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Compound																
1-Methylnaphthalene		30,33				100,33		10,0		10,0	70,33	10,0	10,0			
2-Methylnaphthalene	20,0	30,33	33,0		0,33		33,0	10,0		10,0	70,33	10,33			10,0	20,0
Acenaphthene																
Acenaphthylene	0,50	0,33	0,33	0,33			0,33	0,33	0,33	0,33	0,33	0,33	0,33	0,33		0,33
Anthracene		10,100		0,33	33,33		0,33	20,0	11,0		10,0		10,0	10,0		20,0
Benz[a]anthracene		0,33	0,33		0,33	0,33	0,67	0,33	0,33		0,33			0,33		
Benzo(a)pyrene		10,33	67,33	33,33	0,33	0,33		30,0	11,0			10,33		10,33		40,33
Benzo(b)fluoranthene	0,50	20,67	67,67	67,67	67,67	0,67	0,33	20,67	0,67	0,67	0,33	30,67	20,67	30,67	10,67	30,67
Benzo(ghi)perylene	0,50	20,67	33,33	33,33	33,33	0,33		30,33			0,33	60,33	10,33	10,33	20,22	20,33
Benzo(k)fluoranthene	0,100	20,0	33,67	67,67	67,33	0,33	0,33	20,67	0,67	0,67	0,33	20,67	10,67	10,67	10,67	30,67
Chrysene	10,100	30,33	0,67	33,33	33,33		0,67	0,33	11,0	0,67	0,33	0,67		10,33		0,33
Dibenzo(a,h)anthracene	0,50								0,33							0,33
Fluoranthene		0,33	33,67	0,67	33,67	33,33		10,33	11,67	0,67	10,67	80,67	20,67	10,67	20,67	50,67
Fluorene	10,0	40,0		0,33	33,0			10,0	0,33	20,0	40,33					
Indeno(1,2,3-cd)pyrene	0,100	10,67	33,67	0,67	33,67	0,67	33,67	20,67	0,67	0,67	0,67	20,67	10,0	20,67	20,67	20,67
Naphthalene	10,100	30,100	33,100	33,100	33,100	33,67	0,100	20,100	11,100	20,100	70,100	10,100	0,100	20,100	10,100	30,33
Phenanthrene	80,100	100,100	67,100	100,100	100,100		0,33	70,100	67,100	90,100	100,100	40,100	20,100	50,100	30,100	50,100
Pyrene	10,100	10,67	67,100	67,100	67,100	0,33		40,67	1,67	0,100	20,100	100,100	20,33	20,33	20,67	40,100

* Number in front of comma represents the percentage of events the compound was detected in Round 1; the number after the comma represents the percentage of events the compound was detected in Round 2.

Shading indicates glass control panels.
Panel identification codes are defined in Table 1 on page 25.

methylnaphthalene and phenanthrene. Unlike Round 1, this panel did not differ in number of PAH compounds detected in Round 2 from either of the other two panels of built-up and modified built-up roofing materials (BUR and BUA).

Phthalates

Table 2 in the *Methods* section lists the number of rain events during which Ecology analyzed for phthalates in Rounds 1 and 2 by panel type. During Round 1, Ecology analyzed runoff from all panels for phthalates for rain events 1-3. Thereafter, staff sampled for phthalates on the asphalt-based, the single-ply, and the glass control panels. During Round 2, Ecology sampled phthalates in runoff from all the panels for three rain events (12, 15, and 17).

Concentrations of detected phthalates in runoff from all panels were low. Table 8 lists the number of sampling events the specific phthalate was detected in runoff from each panel. (Appendix B provides data tables.) Table 8 also lists the number of rain events in which phthalates were analyzed in each round. Only those phthalates that were detected above a concentration five times the contamination in the method or equipment rinse blanks are depicted in the table. Those panels not depicted in Table 8 did not have phthalates detected in runoff for any rain event. Di-N-butylphthalate was not detected in samples from any rain event. Di-N-octylphthalate was detected in runoff from the greatest number of panels, but was only detected during Round 1.

Table 8. Percent of sampling events in which a phthalate was detected for both sampling rounds.*

Number of Events Sampled/Round	**Steep-Slope Panels**					**Low-Slope Panels**						
	AS^{A}	**CPR**	**PAZ**	**TWO**	**WOS**	**BUA**	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**GLO**
Round 1	10	3	3	3	3	9	10	10	10	10	10	10
Round 2	3	3	3	3	3	3	3	3	3	3	3	3
Compound												
Bis(2-Ethylhexyl) phthalate	10,0	33,0		100,0	67,0							
Benzyl butylphthalate	20,0										0,33	
Diethyl phthalate			33,0	0,67								20,0
Dimethyl phthalate				33,0					0,33		0,33	10,0
Di-N-butylphthalate												
Di-N-octylphthalate	20,0	33,0		100,0		33,0	90,0	90,0	30,0	10,0		20,0

* Number in front of comma represents the percentage of events in which the compound was detected in Round 1; number after the comma represents the percentage of events the compound was detected in Round 2.
Shading indicates glass control panel.
Panel identification codes are defined in Table 1 on page 25.

During Round 2, phthalates were detected in runoff from only three panels. Runoff from the TPO panel included two phthalates during Round 2, but none during Round 1. Runoff from the treated wood shake (TWO) panel had the greatest number of phthalates detected across all sampled events. This is noteworthy because runoff from the TWO panel was sampled fewer times than the asphalt-based, single-ply, or control panels. The TWO panel was also the only panel in which the runoff had three detections of bis (2 ethylhexyl) phthalate. No bis (2 ethyl hexyl) phthalate was detected in runoff from the treated wood shake panel (TWO) during Round 2.

PBDEs

During Round 1, 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 glass control panels. During Round 2, Ecology sampled PBDEs in runoff from all the panels during three rain events (12, 15, and 17).

During Round 1, PBDE congeners were rarely detected and only at concentrations between the MDL and the reporting limit (RL), with two exceptions. Runoff from the copper (CPR) and wood shingle (WOS) panels had two detections that were above the RL. In Round 2, by contrast, no PBDE congeners were detected above the MDL in runoff from any panel. See data tables in Appendix B.

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Discussion

Rain Event Information

During the first round of the study (between January 29 and April 19, 2013), 313 mm of cumulative precipitation fell on the panels. Of this amount, the study captured and sampled runoff from a total of 106 mm, representing 34% of the amount that fell. The cumulative rainfall during the second round (October 30, 2013 to January 28, 2014) was 253 mm. Of this amount, Round 2 captured and sampled a total of 76 mm or 30% of the rainfall during the period. While the cumulative rainfall was less during Round 2, the proportion sampled compares well with that of Round 1.

The sampled rain events in Round 1 represented between the 52nd and 91st percentile of the typical rainfall in a 24-hour period for this location. During Round 2, the amount of rain that fell during the sampled events expanded the lower end of the range. The Round 2 range of precipitation amounts represented between the 28th and 91st percentile, typical rainfall in a 24-hour period for this location (Howie and Labib, pers. comm., 2012). Capture of lower precipitation amounts was possible because Ecology analyzed for total metals only for seven of the Round 2 rain events, requiring less volume for analysis. The amount of rainfall during Round 1 sampling events was not significantly different (using the Mann Whitney test at $\alpha = 0.05$) from the amount of rainfall during the Round 2 sampling events.

Average rain intensities (mm/hr) ranged between the 40th and 96th percentiles during Round 1 and between the 39th and 79th percentiles during Round 2. The average rain intensities were not statistically different between Round 1 and 2. Figure 9 provides the distribution of the average intensities across both sampling rounds. Figure 10 provides the distribution for the peak intensities (in units of mm/15-minute interval) across all events. The literature often correlates peak intensities and concentration. Noteworthy is the fact that the average intensities and the peak intensities did not generally parallel one another in their distributions. Staff also calculated effective rain intensities only for those 15-minute intervals in which rain fell. Ecology found that the effective intensities in Round 1 were significantly greater than those in Round 2 (using the Mann Whitney test at $\alpha = 0.05$). Ecology subsequently assessed effective intensities for potential correlations with concentration.

The range of antecedent dry conditions in the 6-hour period preceding a sampling event, presented in Table 4, represented the full range of conditions defined by the QA Project Plan (Ecology, 2013a). Precipitation in the 6-hour antecedent dry periods ranged from 0 to nearly 2.5 mm in Round 1, while no precipitation fell in the 6-hour period preceding any rain event during Round 2. Having no precipitation in the 6-hour period preceding an event allowed Ecology to capture the initial flush for all sampling events during Round 2.

During Round 1, the total number of hours with no measurable rain preceding a sampling event ranged from 0 to 66.5 hours. During Round 2, the antecedent dry period ranged from approximately 13 to 141 hours. Figure 11 shows the distribution of antecedent dry periods for all events.

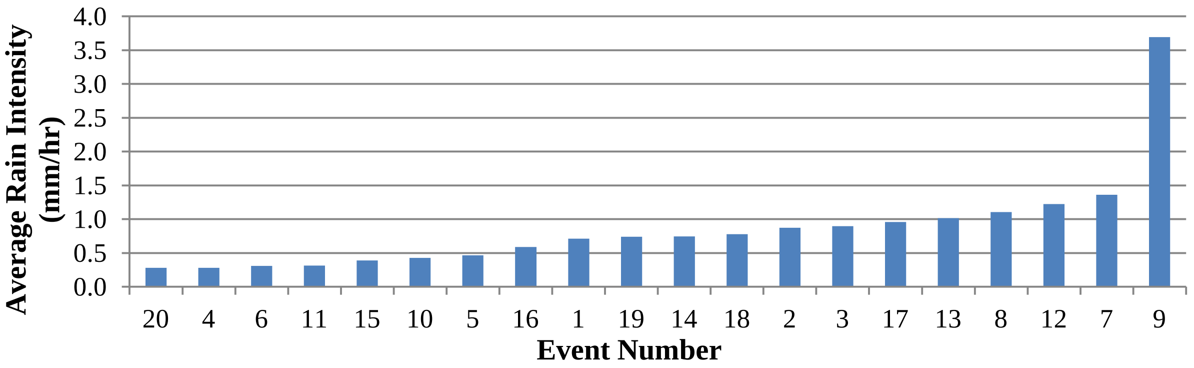


Figure 9. Distribution of average rain intensity (mm/hr) by rain event number.

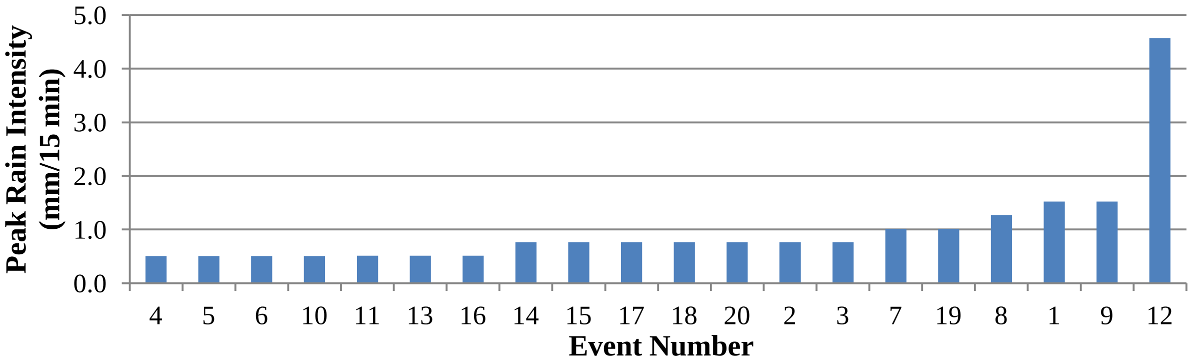


Figure 10. Distribution of peak rain intensity (mm/15 min) by rain event number.

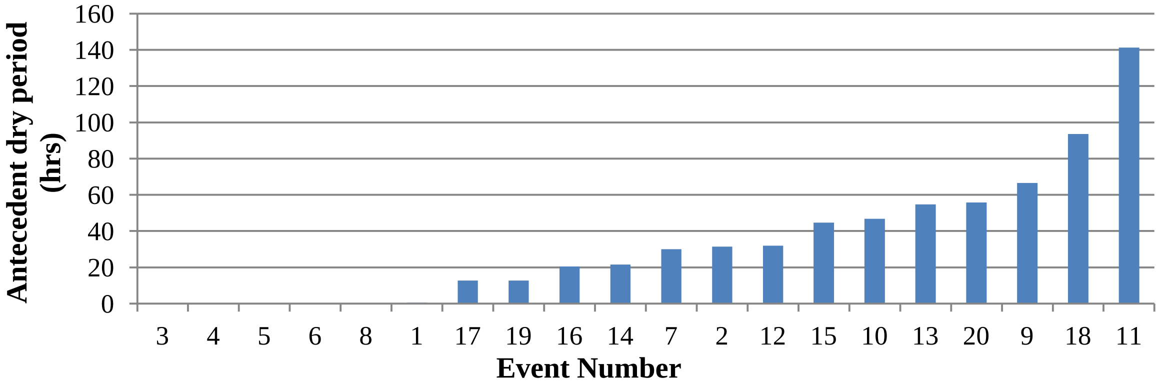


Figure 11. Distribution of antecedent dry period (hours) by rain event number.

The antecedent dry periods in Round 2 were significantly longer than those in Round 1 (using the Mann Whitney test at $\alpha = 0.05$).

Looking at a number of the rain statistics, one should be able to predict a rain event that produced the highest and lowest concentrations for a specific roofing panel, based on literature. Rain event 11 had the longest antecedent dry period, a low precipitation amount, and the lowest effective intensity. One might predict that this event would result in the highest concentrations of metals. Rain event 13 may be similar to rain event 11.

One would expect a rain event with the highest precipitation, the shortest antecedent dry period, and the highest intensities to produce the most dilute sample. No single rain event embodied all of these conditions. However, rain event 7 served as the closest approximation of the other end of the spectrum of observed conditions. Rain event 7 resulted from the third highest precipitation event, an effective intensity in the top one-third of the events measured, and an average antecedent dry period. One might expect the concentrations from rain event 7 to be lower than rain event 11. This topic will be revisited later in the *Discussion* section.

Volumes Recovered

Ecology measured the depth of runoff recovered in each stainless-steel container for each rain event and calculated volumes. For these calculations, staff omitted rain event 5 because the volumes recovered from all roofing panels during rain 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 the very low recovered volume from the concrete tile panel (CTI) during rain event 4 or the asphalt shingle with AR (AAR) in which no volume was recovered, as these two events resulted from improper alignment between the gutter and the collection container.

Figure 12 plots the median sample volume recovered across all panel types versus the precipitation amounts for each of the rain events, except rain event 5. A simple regression performed in Excel resulted in a positive linear relationship with a high correlation coefficient ($r^2 = 0.95$). Rain events 1, 7, and 19 deviated from the regression line (representing 15.51, 18.03, and 12.95 mm precipitation events, respectively). These variations may have resulted from the low resolution of the depth measuring device ($\underline{+}$ 0.5 cm or 0.5 liter).

For each rain 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 9 presents the median percent calculated for each panel across Round 1, Round 2, and both rounds of events.

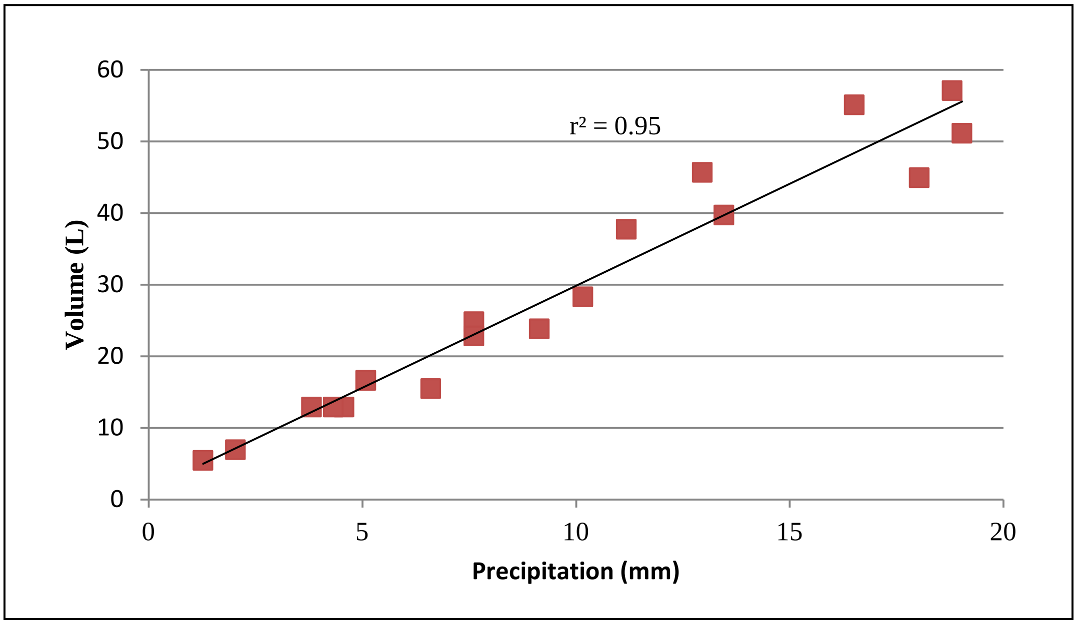


Figure 12. Median sample volume recovered versus precipitation recorded for all sampled events.

Table 9. Median percent theoretical recoveries of panel runoff across rain events.

Panel Type	**Roof ID**	**Percent Recovery**		
		Events 1-10	**Events 11-20**	**Events 1-20**
Asphalt shingle w/ AR	AAR	105	115	105
Asphalt shingle 1	AS1	106	116	106
Asphalt shingle 2	AS2	105	117	106
Asphalt shingle 3	AS3	105	117	106
Copper	CPR	105	115	105
Concrete tile	CTI	106	109	108
Painted galvanized metal	PAZ	105	118	106
Treated wood shake	TWO	105	98	101
Cedar shingle	WOS	103	98	101
Glass steep-slope	GST	107	117	108
Built-up w/ APP	BUA	89	86	86
Built-up	BUR	88	79	82
Built-up w/ SBS	BUS	78	78	78
EPDM	EPD	100	108	100
PVC	PVC	103	108	105
TPO	TPO	100	102	100
Zincalume®	ZIN	100	108	100
Glass low-slope	GLO	104	108	105

Table 9 highlights several noteworthy observations:

- For all panel types, except the built-up roofing, containers recovered 100% or more of the theoretical runoff. In Winters and Graunke (2014), Ecology suggested that this may have been an artifact of the low resolution of the depth measuring device for the receiving containers. However, during Round 2 an observation was made concerning the tipping bucket rain gage: on at least one occasion, staff observed an extremely fine mist for longer than 15 minutes, which did not register on the tipping bucket rain gage. Adequate rainfall may not have accumulated before it evaporated, causing some loss of accuracy.
- Alternatively, some panels may have had greater surface areas than measured, allowing a greater collection surface, depending on the wind conditions.
- The three built-up and modified 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.
- For several panels, a higher percentage of runoff recovery was found than would be predicted on a theoretical basis during Round 2 than during Round 1. This may be attributed to the effects of a greater number of fine mists in Round 2 than in Round 1, triggering fewer tips of the rain gage.
- The wood roofing panels had lower percent recoveries during Round 2. The wood panels may have absorbed some of the initial moisture that fell during these events due to longer Round 2 antecedent dry periods. During Round 1, the antecedent dry periods tended to have some moisture that fell and could have served to hydrate the wood panels, resulting in a greater saturation prior to sample collection in Round 1.

Field Parameters

Ecology used the non-parametric Wilcoxon signed-rank test for statistical comparisons of the field parameters in the roofing panel runoff to the glass control panel runoff. Statisticians recommend use of non-parametric statistical analyses when data violate the assumptions of parametric statistics, such as for stormwater and other environmental data that are not normally distributed. The Wilcoxon signed-rank test compares paired data (e.g., comparing the pH taken in the runoff from two types of roofing materials over the same number of rain events). All statistically significant differences are one-tailed comparisons measured at $\alpha = 0.05$.

pH

Ecology compared the pH values from the roofing panels to the glass control panels using the Wilcoxon signed-rank test. The pH values from rain event 9 were not included in these comparisons, as the pH meter demonstrated substantial drift during that event.

Table 10 provides Round 1 and 2 medians and indicators of statistical differences. Ecology found that the following panels had pH values that were significantly greater than the glass controls during both rounds of sampling:

- Asphalt shingles with AR (AAR)
- Asphalt shingles (AS^A)
- Concrete tile (CTI)
- Modified built-up roofing with APP (BUA)
- Built-up roofing (BUR)
- Modified built-up roofing with SBS (BUS)

Of these, runoff from the concrete tile panel (CTI) had the highest median pH (7.2). The calcium and magnesium matrix of the concrete matrix likely contributed to this pH increase. Median pH values in runoff from the built-up and modified built-up roofing materials (BUA, BUR, and BUS) ranged from 6.0 to 6.7, with BUR the highest.

Runoff from the wood shingle panel (WOS) had pH values significantly less than the glass controls during both rounds of sampling (median of 3.9). For these two panels, the pH of the precipitation was likely reduced by the tannins and lignins in the wood, which are acidic, leaching into the water.

For the copper (CPR), painted galvanized metal (PAZ), treated wood shake (TWO), PVC, and TPO panels, the pH values of the runoff differed from the glass control panels in one round but not in the other as follows:

- The copper (CPR) and painted galvanized metal (PAZ) panels were significantly higher than the glass control only in Round 2.
- The treated wood shake panel (TWO) was significantly lower than the glass control only in Round 2.
- The TPO panel was significantly higher than the glass control only in Round 1.
- The PVC panel was significantly lower than the glass control only in Round 2.

Ecology also evaluated significant differences in the pH of the runoff from each panel between the two rounds using the Mann Whitney test at $\alpha = 0.05$. The asphalt shingle (AS^A) and painted galvanized metal (PAZ) panels had statistically higher pH values in Round 2 than in Round 1 (Table 10).

Table 10. Median pH and specific conductance values in runoff for Rounds 1 and 2 and indicators of significant differences.

Steep-Slope Panels								
	AAR	**AS^{A}**	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**	**GST**
pH[a]								
Round 1 Medians	6.6	6. 8	5.9	7.8	4.9	4.7	3.8	4.8
Round 2 Medians	6.7	7.2	6.2	7.3	5.8	4.6	3.9	4.8
Significant Diff.		a			a			
Specific Conductance (us/cm)								
Round 1 Medians	11	11	4	62	5	12	80	2
Round 2 Medians	13	17	2	63	0	12	54	0
Significant Diff.		a					*	
Low-Slope Panels								
	BUA	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
pH[a]								
Round 1 Medians	6.1	6.6	7.1	4. 6	5	5.8	5.2	5
Round 2 Medians	5.9	6.7	6.3	5.0	4.8	5.3	5.4	5.4
Significant Diff.								
Specific Conductance (us/cm)								
Round 1 Medians	4	9	8	9	3	3	3	1
Round 2 Medians	2	14	0	1	2	2	1	0
Significant Diff.								

[a] Rain event 9 pH data not included in median due to pH meter drift.
Yellow shading indicates panel significantly higher than the glass control at α = 0.05.
Green shading indicates panel significantly lower than the glass control at α = 0.05.
* Round 1 significantly greater than Round 2 at α = 0.05.
a Round 2 significantly greater than Round 1 at α = 0.05.
Dark gray shading indicates glass control panels.
Panel identification codes are defined in Table 1 on page 25.

Specific Conductance

Ecology used the Wilcoxon signed-rank test to assess differences between the specific conductance in runoff from the roofing panels and the glass control panels. Table 10 provides Rounds 1 and 2 median values and indicators of statistical differences. Ecology found that runoff in the following panels had significantly higher conductance values than in the glass controls during both rounds of sampling:

- Asphalt shingles with AR (AAR)
- Asphalt shingles (AS^A)
- Concrete tile (CTI)
- Treated wood shake (TWO)
- Wood shingle (WOS)
- Built-up roofing (BUR)
- EPDM (EPD)

Runoff from the TPO panel had significantly higher specific conductance values than runoff from the glass control in Round 2 but not in Round 1.

Ions and solutes which contribute to elevated conductance values may be expected to be in the runoff from the concrete tile (calcium and magnesium) and the wood (tannins and lignins). Ions may also have originated from either the granular materials on the asphalt-based roofing materials (AAR, AS^A and BUR) or the asphalt. Because the specific conductance values in runoff from the two modified built-up roofing panels (BUS and BUA) were not significantly elevated over the glass panels, the granules are less likely contributors than asphalt. Both modified built-up roofing panels (BUS and BUA) have polymer additives which may prevent leaching from the asphalt.

Ecology also evaluated significant differences in conductance of the runoff between the two rounds for each panel, using the Mann Whitney test. This showed that runoff from the asphalt shingle panels (AS^A) had higher conductance during Round 2, while runoff from the wood panel (WOS) had significantly lower specific conductance values during Round 2.

Total Metals

Analyses of Total Metals in Runoff

Ecology evaluated the concentrations of total metals in runoff from the roofing materials, using box and whiskers plots, across all 20 rain events for each of the five metals. Ecology created box plots using R version 2.15.2 (R Core Team, 2012). The box plots (Figures 13, 15, 17, 19, and 21), particularly when plotted on the log scale, enable one to quickly identify differences between roofing materials for each of the metals.

The steep-slope panels (as defined in Table 1) are listed across the upper x-axis and the low-slope panels are listed across the middle x-axis.

The thicker center line of each box represents the 50th percentile (i.e., the median), and 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.

An asterisk above a box and whisker indicates a statistically significant difference between the panel identified and the appropriate glass control panel (GST for steep-slope or GLO for low-slope). Ecology used the non-parametric Wilcoxon signed-rank test for statistical comparisons of roofing panel runoff to glass control runoff concentrations. Statisticians recommend use of non-parametric statistical analyses when data violate the assumptions of parametric statistics, such as for stormwater and other environmental data that are not normally distributed. The Wilcoxon signed-rank test compares paired data (i.e., comparing the concentrations of a metal in runoff from two types of roofing materials across the same rain events). In this case comparisons were made between the runoff from a roofing panel and the glass control across all 20 rain events. All statistically significant differences identified in Figures 13, 15, 17, 19, and 21 are one-tailed comparisons measured at $\alpha = 0.05$.

The Wilcoxon signed-rank test is also useful for statistical comparisons of non-detected data. Helsel (2005) indicates that standard nonparametric tests such as the signed-rank tests used to compare metals concentrations in runoff can be calculated by assigning the non-detected values a value below the detection limit and less that the lowest observation. "The ranks will efficiently capture the information in the data including the proportion of nondetects, accurately representing what is known about the data. Test results are reliable, not based on '*information*' that is not known, and not dependant on the substitution of arbitrary values." (Helsel, 2005).

Ecology also used box plots to compare results of the first sampling round (rain events 1-10) with results from the second sampling round (rain events 11-20). Ecology made these statistical comparisons of Round 1 versus Round 2 results using non-parametric statistics. Helsel and Hirsch (2002) recommend use of the Mann Whitney test for step trends in which the gap between the two sampling periods is more than about one-third of the entire period of data collection. Since the gap between the end of Round 1 sampling and the beginning of Round 2 sampling was six and a half months, and the total sampling period extended just under a year, Ecology elected to use the Mann Whitney test. All significant differences identified in the following subsections are one-tailed comparisons measured at $\alpha = 0.05$.

For comparisons of runoff concentrations from the same panel from Round 1 to concentrations from Round 2, Ecology subtracted the glass control panel concentration from the roofing panel concentration on an event-by-event basis. This eliminated the possibility of finding significant differences when the concentrations in runoff from the glass controls masked the roofing panel runoff concentrations.

Arsenic

Total arsenic concentrations from most of the roofing panels were low, with a few exceptions. 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 (Table 11).

The box and whiskers plot (Figure 13) shows variability for each panel across the rain events.

Table 11. Total arsenic concentrations (ug/L): median, maximum, minimum, and statistical comparison to glass control across both sampling rounds.

Parameter	Steep-Slope Panels							
	AAR	AS^A	CPR	CTI	PAZ	TWO	WOS	GST
Median	**0.21**	**0.08**	**0.05**	**0.35**	**0.07**	**1,385**	**0.12**	**0.07**
Maximum	**2.96**	**0.35**	**1.40**	**1.19**	**0.28**	**4,690**	**1.00**	**0.70**
Minimum	**0.04**	**0.02**	**0.02**	**0.18**	**0.02**	**72**	**0.02**	**0.02**
Significant Diff.	*			*		*	*	
Parameter	**Low-Slope Panels**							
	BUA	BUR	BUS	EPD	PVC	TPO	ZIN	GLO
Median	**0.06**	**0.08**	**0.10**	**0.07**	**21**	**0.06**	**0.08**	**0.08**
Maximum	**0.21**	**0.38**	**0.49**	**0.24**	**117**	**0.25**	**0.81**	**0.34**
Minimum	**0.02**	**0.02**	**0.02**	**0.02**	**0.97**	**0.02**	**0.02**	**0.02**
Significant Diff.					*			

* Yellow highlight indicates statistically higher than glass control.
Bold indicates analyte detected at or above the MDL.
Dark gray shading indicates glass control panels.
Panel identification codes are defined in Table 1 on page 25.

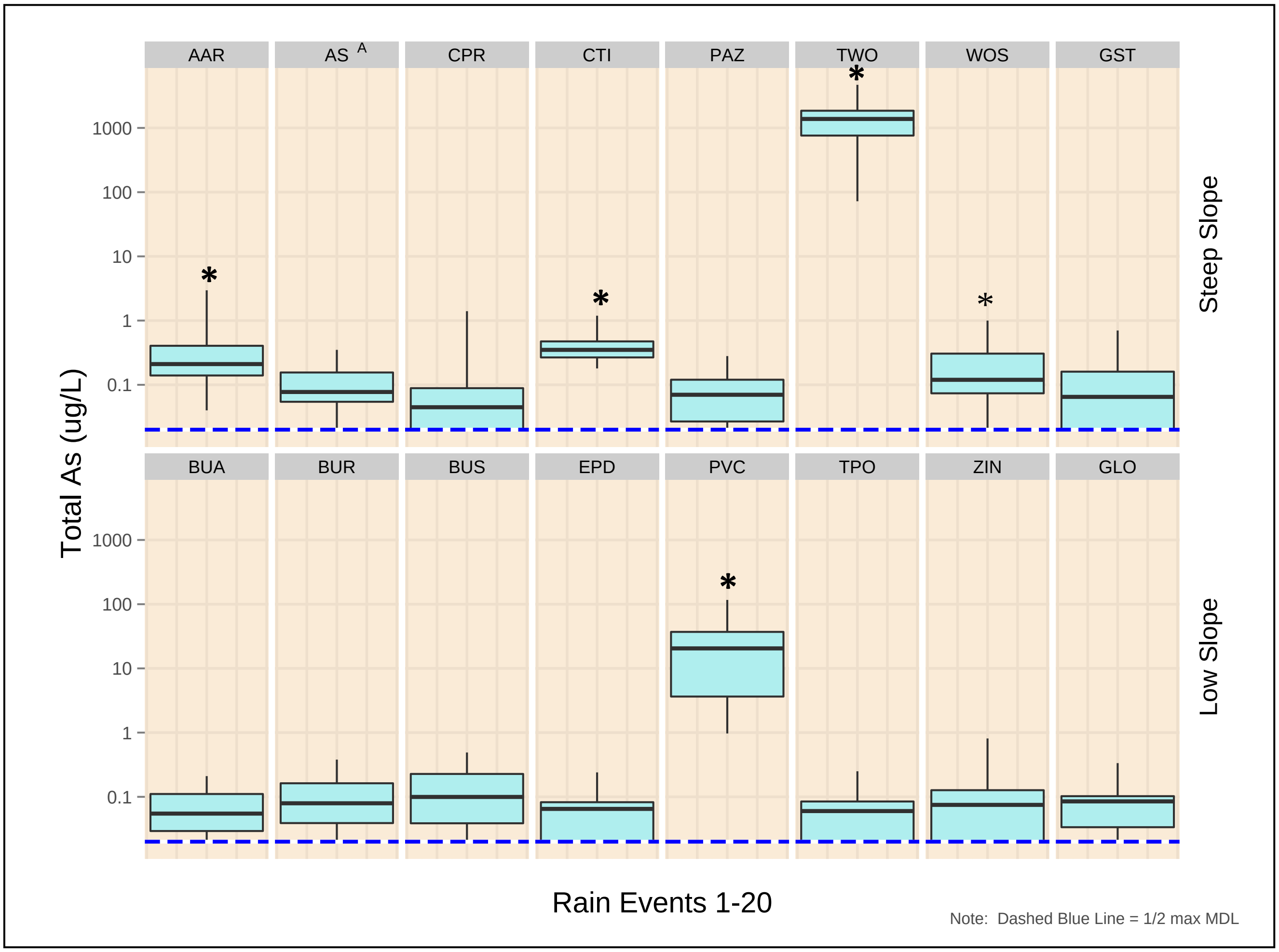


Figure 13. Box plots for total arsenic concentrations across all panels.

* Runoff concentrations were statistically higher than those from the glass control panel.
Panel identification codes are defined in Table 1 on page 25.

Ecology made comparisons between the roofing panels and the glass control panels across all 20 events. The CCA-treated wood shake panel (TWO) consistently released the highest concentrations of arsenic. Total arsenic from this panel ranged in concentration from 72 to 4,690 ug/L with a median concentration of 1,385 ug/L. The treated wood shake panel (TWO) released significantly higher concentrations of total arsenic than the steep-slope glass control panel (GST) across all events.

The PVC panel released the second highest concentrations of arsenic (median value of 21 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 1 and 117 ug/L. The concentration of total arsenic in runoff from the PVC panel was also significantly higher than the low-slope glass control panel (GLO). Arsenic in the runoff may have been attributable to its use as a biocide in the PVC formulation (RTF, pers. comm., 2013).

Three additional panels released total arsenic at concentrations significantly higher than the control panels over the 20 rain events. The asphalt shingle with AR (AAR), wood shingle (WOS), and concrete tile (CTI) panels were all significantly higher than the steep-slope glass control (GST) (Figure 13). As indicated in Table 11, the maximum concentrations of arsenic released from these three panels ranged from 1.0 to 2.96 ug/L.

To assess differences between the two sampling rounds, Ecology compared total arsenic concentrations by panel type for Round 1 (Events 1-10) and Round 2 (Events 11-20). Table 12 shows the medians and results of these comparisons. Figure 14 provides box and whiskers plots that visually depict differences.

Table 12. Comparisons of Round 1 and 2 median total arsenic concentrations (ug/L).

Round	**Steep-Slope Panels**							
	AAR	**AS^{A}**	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**	**GST**
Round 1	**0.40**	**0.10**	**0.05**	**0.35**	**0.09**	**1,610**	**0.26**	**0.12**
Round 2	**0.15**	**0.06**	**0.04**	**0.37**	**0.04**	**932**	**0.09**	0.02
Significant Difference						*		*
Round	**Low-Slope Panels**							
	BUA	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
Round 1	**0.07**	**0.10**	**0.18**	**0.02**	**38**	**0.08**	**0.11**	**0.10**
Round 2	**0.05**	**0.05**	**0.05**	**0.07**	**3.6**	**0.03**	**0.05**	**0.05**
Significant Difference					*			*

* Yellow shading means a statistically lower concentration of total arsenic released in Round 2.
Bold indicates analyte detected at or above the MDL.
Dark gray shading indicates glass control panels.
Panel identification codes are defined in Table 1 on page 25.

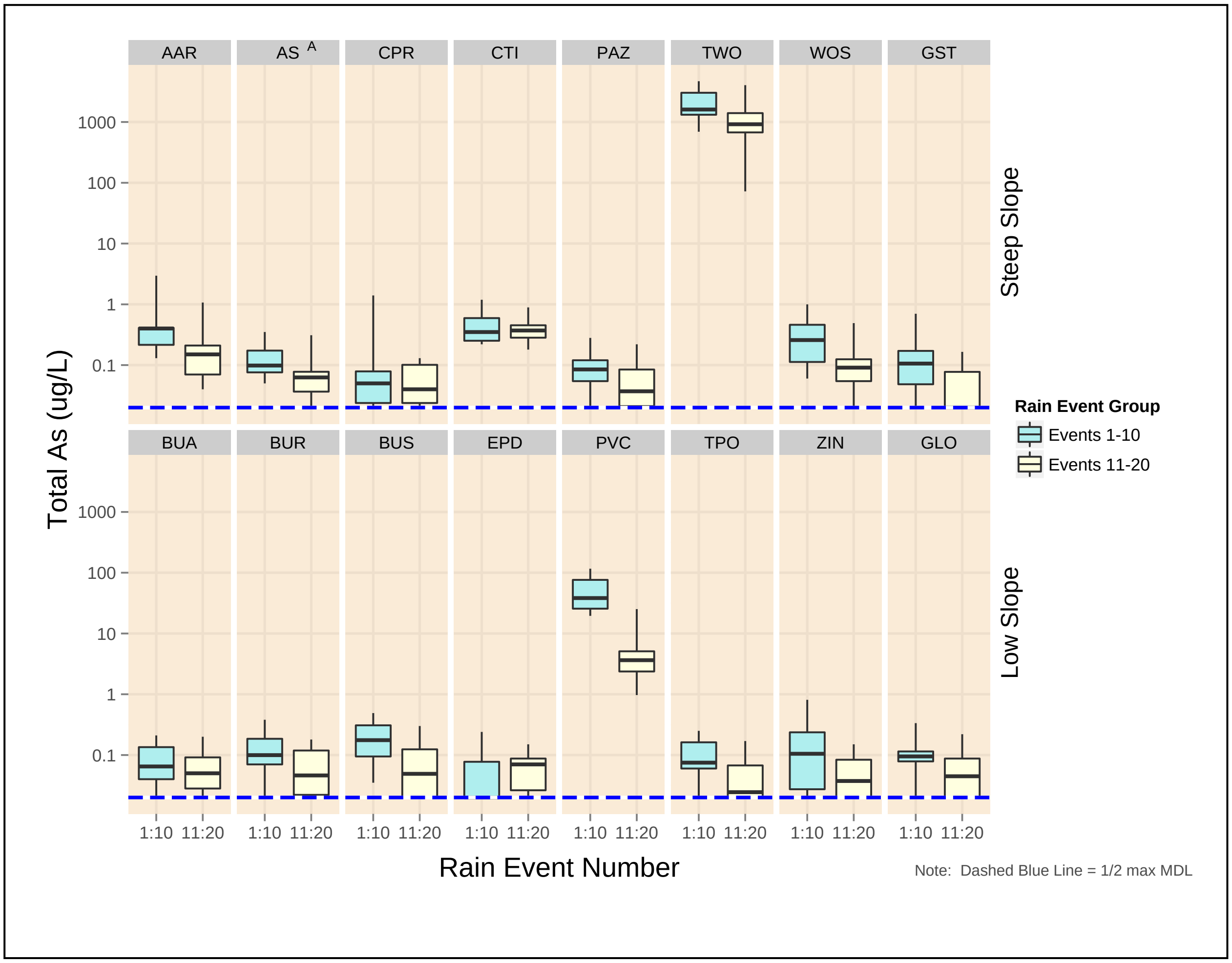


Figure 14. Box plots comparing total arsenic concentrations from rain events 1-10 to rain events 11-20.

Panel identification codes are defined in Table 1 on page 25.

Ecology found the greatest, and statistically significant, declines between the two rounds in the treated wood shake (TWO) and PVC panels. Table 12 also identifies the arsenic in runoff from the two glass control panels as statistically lower in Round 2.

Cadmium

Total cadmium concentration in runoff from all roofing panels approached the limits of detection. Cadmium concentrations in runoff ranged from non-detected values for the majority of both steep- and low-slope panels to detections just above the MDL. Table 13 lists the median, maximum, and minimum concentrations released from each of the panels over the 20 sampling events. Where the median values were not detected, Table 13 lists a value of one-half the MDL.

Table 13. Total cadmium concentrations (ug/L): median, maximum, minimum, and statistical comparison to glass control across both sampling rounds.

Parameter	**Steep-Slope Panels**							
	AAR	**AS[A]**	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**	**GST**
Median	0.005	0.005	**0.015**	0.005	0.005	**0.105**	0.005	0.005
Maximum	**0.10**	**0.02**	**0.06**	**0.04**	**0.03**	**0.31**	**0.02**	**0.03**
Minimum	0.005	0.005	0.005	0.005	0.005	**0.050**	0.005	0.005
Significant Diff.						*		

Parameter	**Low-Slope Panels**							
	BUA	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
Median	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
Maximum	**0.02**	**0.02**	**0.09**	**0.04**	**0.03**	**0.04**	**0.03**	**0.03**
Minimum	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
Significant Diff.								

* Yellow highlight indicates statistically higher than glass control.
Bold indicates analyte detected at or above the MDL.
Dark gray shading indicates glass control panels.
Panel identification codes are defined in Table 1 on page 25.

Figure 15 presents the box plots by panel type for all 20 rain events. The treated wood shake panel (TWO) consistently had the highest measurable concentrations of cadmium, ranging between 0.05 and 0.31 ug/L. Using the Wilcoxon signed-rank test, Ecology found that cadmium concentrations in runoff from the treated wood shake panel (TWO) were significantly higher than those from the steep-slope glass control panel (GST). The cadmium concentrations in runoff from the copper panel (CPR) were significantly higher than the glass control during Round 1, but concentrations could not be distinguished from the glass control in Round 2. Thus, Table 13 does not reflect a significantly higher concentration across both rounds.

Concentrations of cadmium in runoff from the other roofing panels were similar to those in runoff from the glass control panels. Ecology found no other statistical differences.

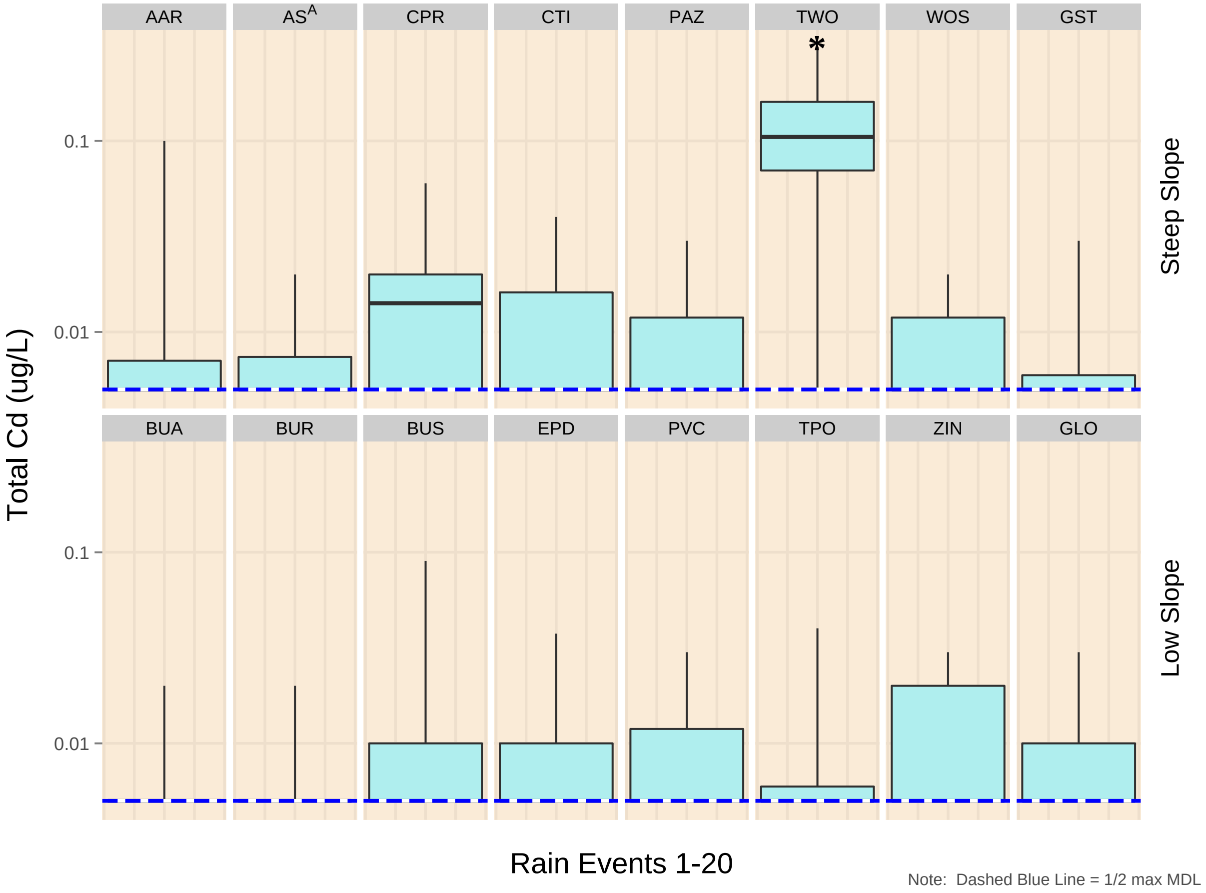


Figure 15. Box plots for total cadmium concentrations across all panels.

* Runoff concentrations were statistically higher than those from the glass control panel.
Panel identification codes are defined in Table 1 on page 25.

To assess differences between the two sampling rounds, Ecology used the Mann Whitney test to compare cadmium concentrations in runoff from each panel during Round 1 to those measured during Round 2. Table 14 shows the medians and results of these comparisons. Figure 14 provides box plots that visually depict differences.

Ecology found significantly lower cadmium concentrations in Round 2 than in Round 1 for the treated wood shake (TWO) panel (Table 14). The Mann Whitney analysis was inconclusive for the copper panel (CPR) because cadmium concentrations in Round 1 were differentiable from the glass controls, while those in Round 2 were generally not.

Overall, the new roofing materials evaluated do not appear to be substantial contributors of cadmium in roof runoff.

Table 14. Comparisons of Rounds 1 and 2 median total cadmium concentrations (ug/L).

Round	Steep-Slope Panels							
	AAR	**AS^A**	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**	**GST**
Round 1	0.005	**0.007**	**0.020**	0.005	**0.010**	**0.135**	0.005	0.005
Round 2	0.005	0.005	**0.006**	**0.010**	0.005	**0.095**	0.005	0.005
Significant Difference						*		
Round	**Low-Slope Panels**							
	BUA	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
Round 1	0.005	0.005	**0.008**	0.005	0.005	0.005	**0.008**	0.005
Round 2	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
Significant Difference								

* Yellow shading means a statistically lower concentration of total cadmium released in Round 2.
Bold indicates analyte detected at or above the MDL.
Dark gray shading indicates glass control panels.
Panel identification codes are defined in Table 1 on page 25.

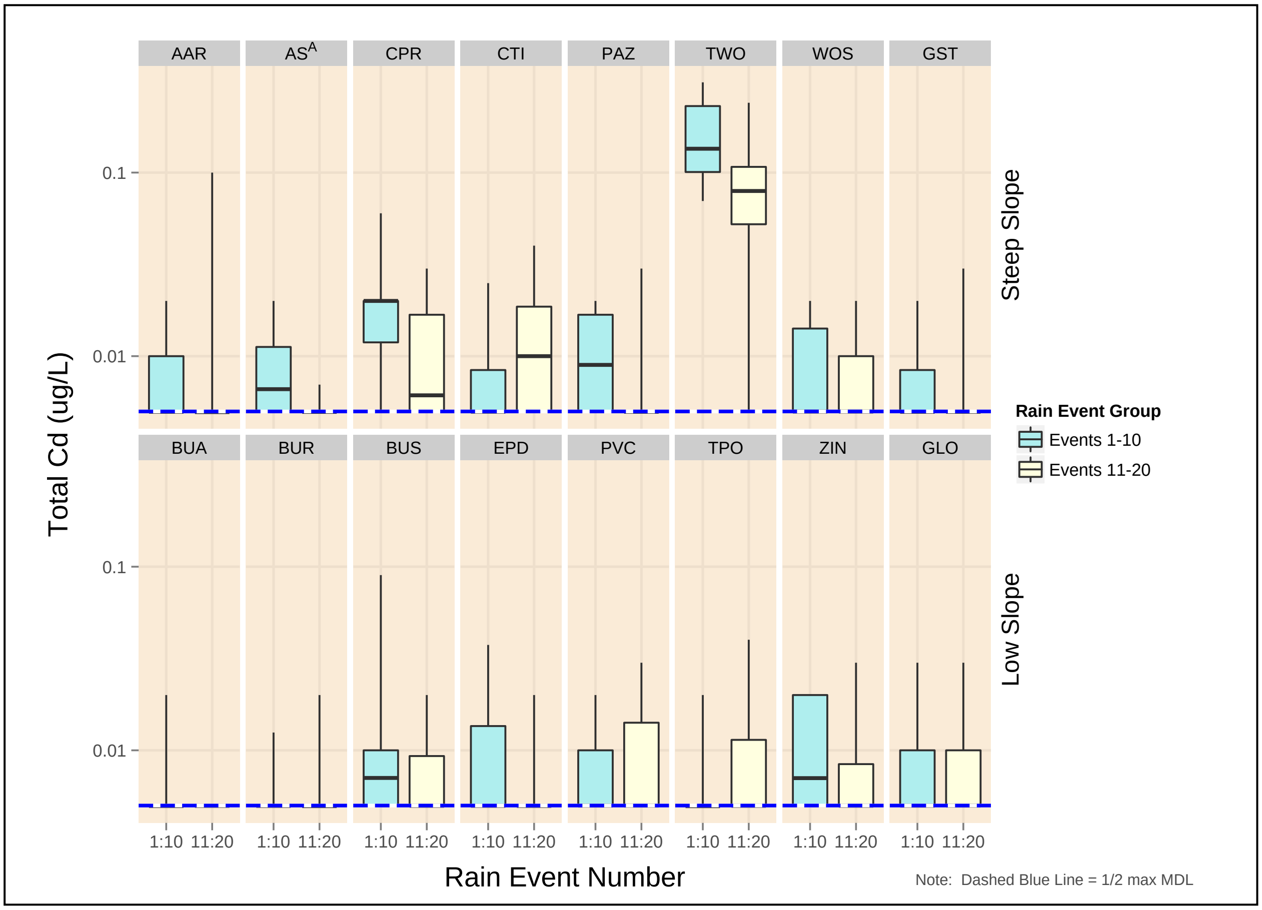


Figure 16. Box plots comparing total cadmium concentrations from rain events 1-10 to rain events 11-20.

Panel identification codes are defined in Table 1 on page 25.

Copper

Total copper concentrations in runoff from the panels varied widely among the panels. Table 15 provides the median, maximum, and minimum values for each roofing panel and the glass control panels.

The copper (CPR) and the treated wood shake (TWO) panels released the highest concentrations of copper. The copper concentrations in runoff from the treated wood shake panel ranged from 262 to 3,190 ug/L (with a median of 825 ug/L), while concentrations from the copper panel ranged from 1,035 to 4,220 ug/L (with a median of 1,905 ug/L). The asphalt shingle panel with AR (AAR) and the replicate asphalt shingle (AS^A) panel released much lower concentrations than either the copper or the treated wood shake panels.

Table 15. Total copper concentrations (ug/L): median, maximum, minimum, and statistical comparison to glass control across both sampling rounds.

Parameter	Steep-Slope Panels							
	AAR	**AS^A**	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**	**GST**
Median	**30**	**2.1**	**1,905**	**0.63**	**0.56**	**825**	**0.74**	**0.40**
Max	**193**	**11**	**4,220**	**2.4**	**2.5**	**3,190**	**2.4**	**4.1**
Min	**8.4**	**0.38**	**1,035**	**0.25**	**0.20**	**262**	**0.33**	**0.15**
Significant Diff.	*	*	*			*		
Parameter	**Low-Slope Panels**							
	BUA	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
Median	**0.51**	**0.46**	**0.37**	**0.38**	**0.43**	**0.48**	**0.50**	**0.46**
Max	**2.7**	**1.4**	**1.9**	**1.2**	**1.8**	**1.8**	**2.5**	**2.5**
Min	**0.15**	**0.07**	**0.12**	**0.16**	**0.16**	**0.25**	**0.16**	**0.16**
Significant. Diff.								

* Yellow highlight indicates statistically higher than glass control.
Bold indicates analyte detected at or above the MDL.
Dark gray shading indicates glass control panels.
Panel identification codes are defined in Table 1 on page 25.

The box plot (Figure 17) also shows that the copper panel (CPR) and the treated wood shake panel (TWO) had the highest measured copper concentrations in runoff. Both of these panels released statistically higher copper concentrations than the glass control panel. Additionally, the asphalt shingle with AR (AAR) and the asphalt shingle replicate (AS^A) panels released statistically higher concentrations of copper than the steep-slope glass control panel. Copper concentrations in runoff from the low-slope panels did not differ significantly from the glass control panel.

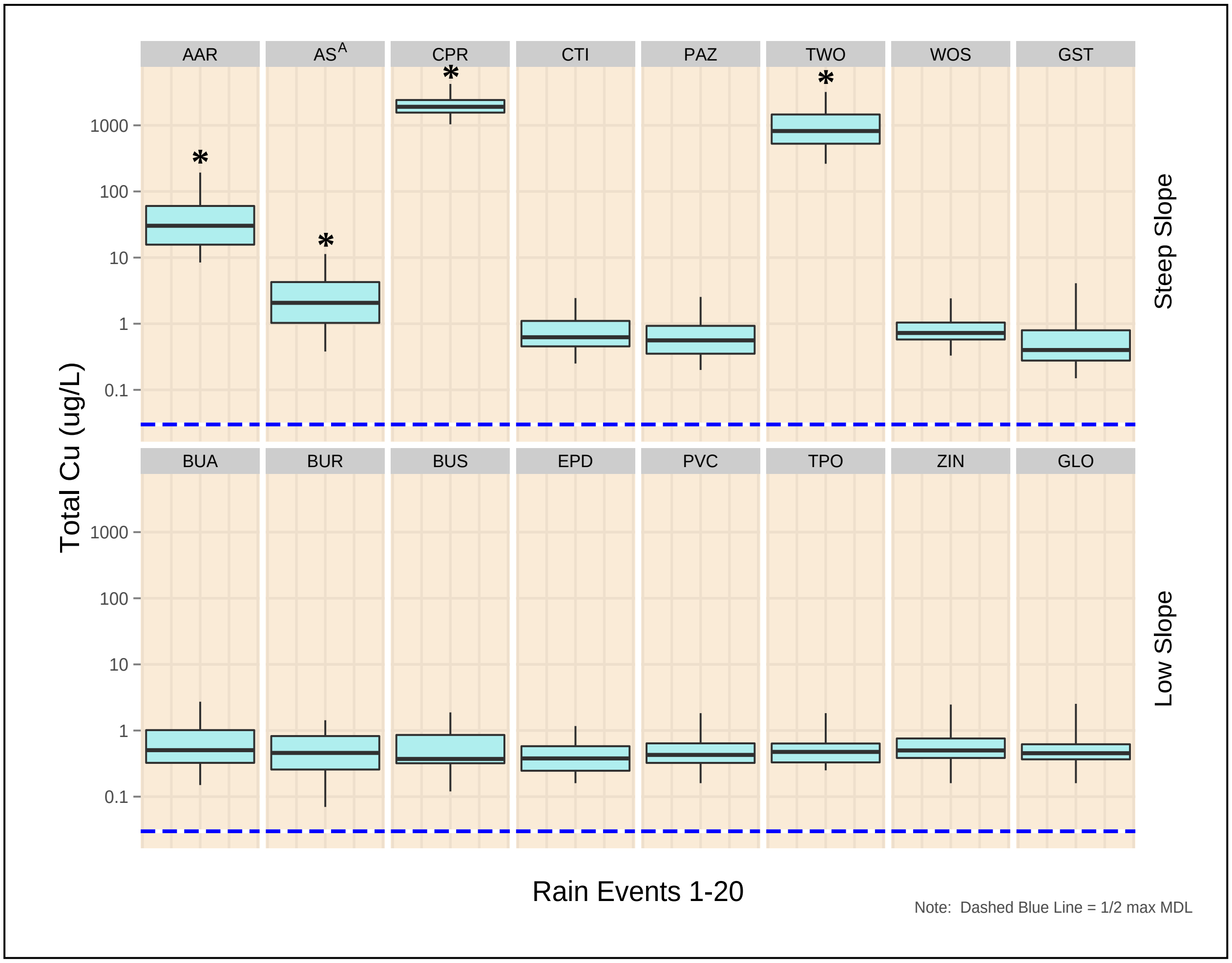


Figure 17. Box plots for total copper concentrations across all panels.

* Runoff concentrations were statistically higher than those from the glass control panel.
Panel identification codes are defined in Table 1 on page 25.

During Round 1 of sampling, the three replicated asphalt shingle panels (AS^A) displayed differences in the concentrations of copper released. As described in Winters and Graunke (2014), AS-3 released a significantly higher concentration of copper than AS-2 at $\alpha = 0.05$. No other significant differences existed among the three replicates. During Round 2, the differences among the copper concentrations in runoff from these three replicates diminished to insignificant. The higher copper released to runoff from AS-3 in Round 1 was short-lived, implying that the higher copper concentrations found in the one row of shingles had leached out by Round 2.

Ecology calculated the median total copper concentration by panel type for each of the two rounds of sampling (Table 16) and used box plots to visually depict the differences (Figure 18).

Table 16. Comparisons of Rounds 1 and 2 median total copper concentrations (ug/L).

Round	**Steep-Slope Panels**							
	AAR	**AS^A**	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**	**GST**
Round 1	**32**	**3.6**	**1,708**	**0.53**	**0.48**	**1,263**	**0.78**	**0.35**
Round 2	**30**	**1.17**	**1,985**	**0.83**	**0.56**	**520**	**0.74**	**0.43**
Significant Diff.		*				*		
Round	**Low-Slope Panels**							
	BUA	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
Round 1	**0.43**	**0.29**	**0.37**	**0.44**	**0.43**	**0.40**	**0.45**	**0.39**
Round 2	**0.53**	**0.55**	**0.43**	**0.34**	**0.44**	**0.51**	**0.51**	**0.52**
Significant Diff.								

* Yellow shading means a statistically lower concentration of total copper released in Round 2.
Bold indicates analyte detected at or above the MDL.
Dark gray shading indicates glass control panels.
Panel identification codes are defined in Table 1 on page 25.

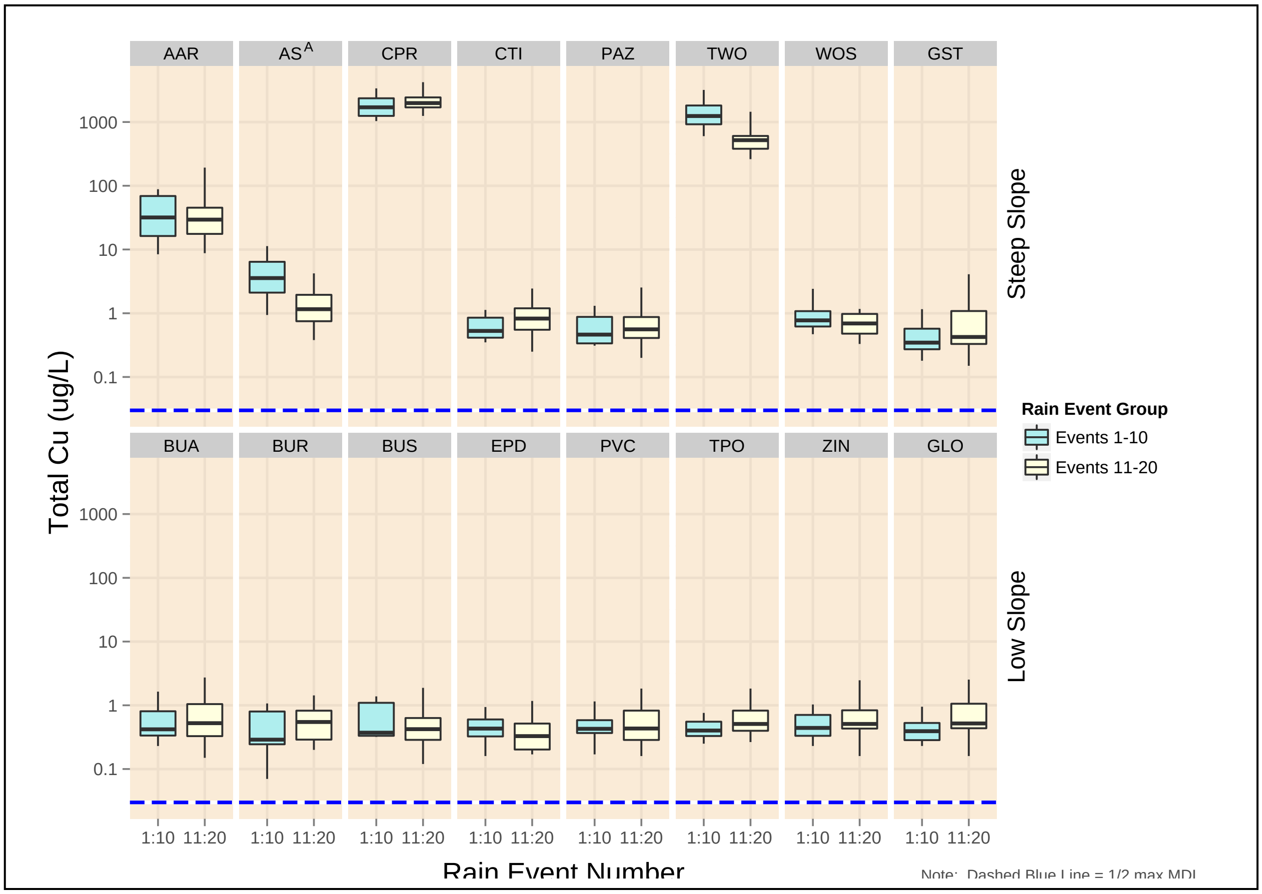


Figure 18. Box plots comparing total copper concentrations from rain events 1-10 to rain events 11-20.

Panel identification codes are defined in Table 1 on page 25.

Using the Mann Whitney test to compare concentrations between the two rounds, Ecology found the treated wood shake (TWO) and the asphalt shingle (AS^A) panels released significantly lower concentrations of copper during Round 2 (Table 16).

No other roofing materials displayed significant differences in copper concentrations between the two sampling rounds. While the median copper concentrations in runoff from the asphalt shingle panel with AR (AAR) declined between Round 1 and Round 2 (Table 16), the decline was not significant at $\alpha = 0.05$.

Lead

Lead concentrations released from the panels varied across all roofing materials but were consistently low, as evidenced in Table 17 and Figure 19. Lead concentrations in runoff ranged from the MDL for the asphalt shingle with AR panel (AAR) to a maximum of 2.36 ug/L from the concrete tile panel (CTI). Median values ranged from 0.03 to 0.32 ug/L. Table 17 lists the median, minimum, and maximum concentrations released from each of the panels over the 20 events.

The Wilcoxon analysis indicated that the concrete tile panel (CTI) released significantly higher lead concentrations to runoff than the glass control (GST). On the other hand, lead concentrations in runoff from the glass control panels (GST and GLO) were significantly higher than in runoff from several of the roofing panels, as depicted in Figure 19, including:

- Asphalt shingle with AR (AAR)
- Treated wood shake panel (TWO)
- Wood shingle (WOS)
- Three built-up and modified-built up roofing panels (BUA, BUR, and BUS).

Table 17. Total lead concentrations (ug/L): median, maximum, minimum, and statistical comparison to glass control across both sampling rounds.

Parameter	**Steep-Slope Panels**							
	AAR	**AS^{A}**	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**	**GST**
Median	**0.05**	**0.06**	**0.22**	**0.32**	**0.18**	**0.03**	**0.04**	**0.14**
Maximum	**0.16**	**1.1**	**0.67**	**2.36**	**0.46**	**0.26**	**0.13**	**1.3**
Minimum	0.002	**0.01**	**0.10**	**0.11**	**0.04**	0.002	**0.006**	**0.04**
Significant Diff.	[a]			*		[a]	[a]	
Parameter	**Low-Slope Panels**							
	BUA	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
Median	**0.03**	**0.04**	**0.04**	**0.13**	**0.17**	**0.12**	**0.18**	**0.17**
Maximum	**0.11**	**0.22**	**0.08**	**0.54**	**0.37**	**0.39**	**0.41**	**0.68**
Minimum	0.002	0.002	0.002	0.002	**0.04**	**0.04**	**0.05**	**0.05**
Significant Diff.	[a]	[a]	[a]					

* Yellow highlight indicates statistically higher than glass control.
[a] Yellow highlight indicates statistically lower than glass control.
Bold indicates analyte detected at or above the MDL.
Dark gray shading indicates glass control panels.
Panel identification codes are defined in Table 1 on page 25.

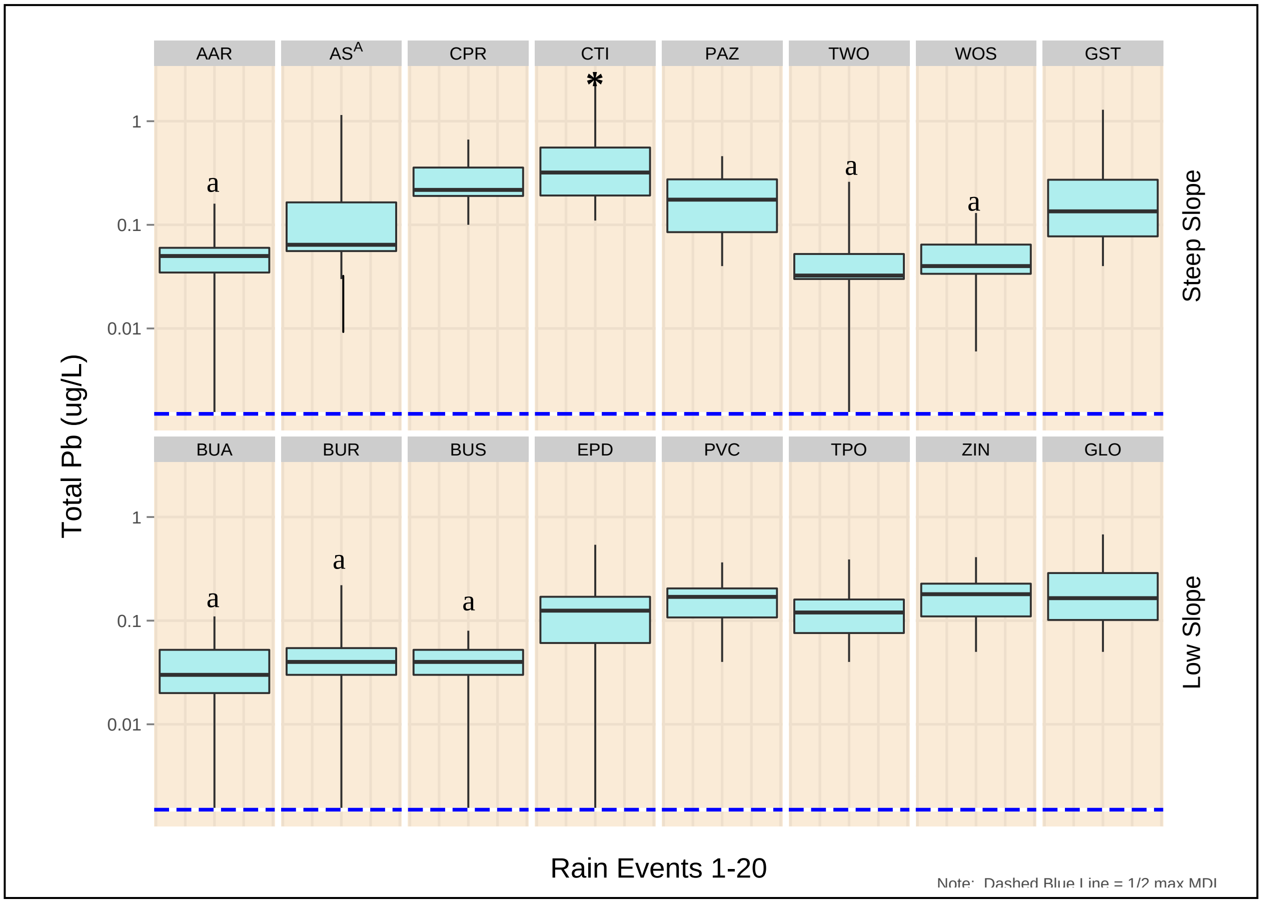


Figure 19. Box plots for total lead concentrations across all panels.

a Runoff concentration from panel was significantly lower than from the glass control panel.
* Runoff concentrations were statistically higher than those from the glass control panel.
Panel identification codes are defined in Table 1 on page 25.

This implies that the lead in the control panels (GST and GLO) may have leached from the glass. Except for the concrete tile panel (CTI), the roofing materials evaluated did not release lead to runoff.

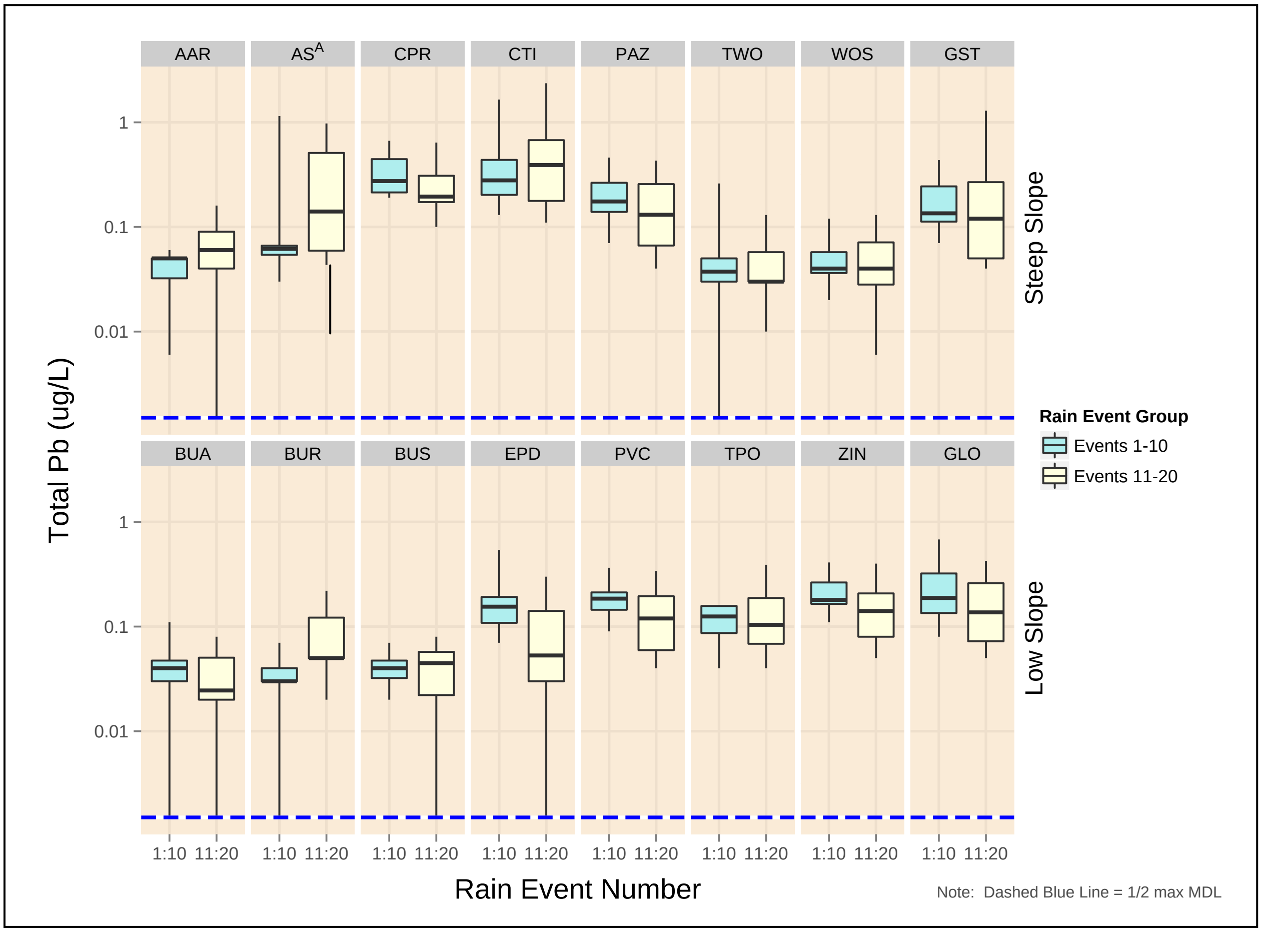
Ecology calculated the median total lead concentration by panel type for each of the two sampling rounds (Table 18), and Ecology prepared box plots to visually depict the differences (Figure 20).

Ecology compared lead concentrations in runoff in Round 1 with those in Round 2 using the Mann Whitney test and found no statistically significant declines (Table 18). Although lead concentrations in runoff from the EPDM panel (EPD) appeared to be higher in Round 1 than 2, insufficient numbers of values were available for comparison after the glass control concentrations were subtracted.

Table 18. Comparisons of Rounds 1 and 2 median total lead concentrations (ug/L).

Round	**Steep-Slope Panels**							
	AAR	**AS[A]**	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**	**GST**
Round 1	**0.05**	**0.06**	**0.28**	**0.28**	**0.18**	**0.04**	**0.04**	**0.14**
Round 2	**0.06**	**0.07**	**0.20**	**0.39**	**0.14**	**0.03**	**0.04**	**0.13**
Significant Diff.								
Round	**Low-Slope Panels**							
	BUA	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
Round 1	**0.04**	**0.03**	**0.04**	**0.16**	**0.19**	**0.13**	**0.18**	**0.19**
Round 2	**0.03**	**0.05**	**0.05**	**0.06**	**0.12**	**0.11**	**0.15**	**0.14**
Significant Diff.								

* Yellow shading means a statistically lower concentration of total lead released in Round 2.
Bold indicates analyte detected at or above the MDL.
Gray shading indicates glass control panels.
Panel identification codes are defined in Table 1 on page 25.



Note: Dashed Blue Line = 1/2 max MDL

Figure 20. Box plots comparing total lead concentrations from rain events 1-10 to rain events 11-20.

Panel identification codes are defined in Table 1 on page 25.

Zinc

Ecology found measurable concentrations of total zinc in runoff from all roofing panels during every rain event. Ecology calculated the median, maximum, and minimum concentrations of zinc in runoff from each of the panels across all 20 rain events (Table 19).

Table 19. Total zinc concentrations (ug/L): median, maximum, minimum, and statistical comparison to glass controls across both sampling rounds.

Parameter	**Steep-Slope Panels**							
	AAR	**AS**[A]	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**	**GST**
Median	**6.4**	**2.7**	**4.0**	**4.3**	**52**	**8.8**	**5.6**	**3.7**
Maximum	**19**	**6.9**	**12**	**12**	**194**	**26**	**17**	**13**
Minimum	**1.7**	**0.9**	**1.1**	**1.1**	**18**	**2.9**	**1.2**	**1.0**
Significant Diff.					*	*		
Parameter	**Low-Slope Panels**							
	BUA	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
Median	**2.9**	**2.5**	**2.5**	**57**	**5.1**	**3.5**	**114**	**4.1**
Maximum	**9.0**	**6.3**	**6.1**	**313**	**12**	**15**	**578**	**9.8**
Minimum	**0.8**	**0.9**	**0.5**	**15**	**1.4**	**2.0**	**38**	**1.2**
Significant Diff.				*	*		*	

[A] Average of three replicate asphalt shingle panels.
* Yellow highlight indicates statistically higher than glass control.
Bold indicates analyte detected at or above the MDL.
Dark gray shading indicates glass control panels.
Panel identification codes are defined in Table 1 on page 25.

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) (Figure 21).

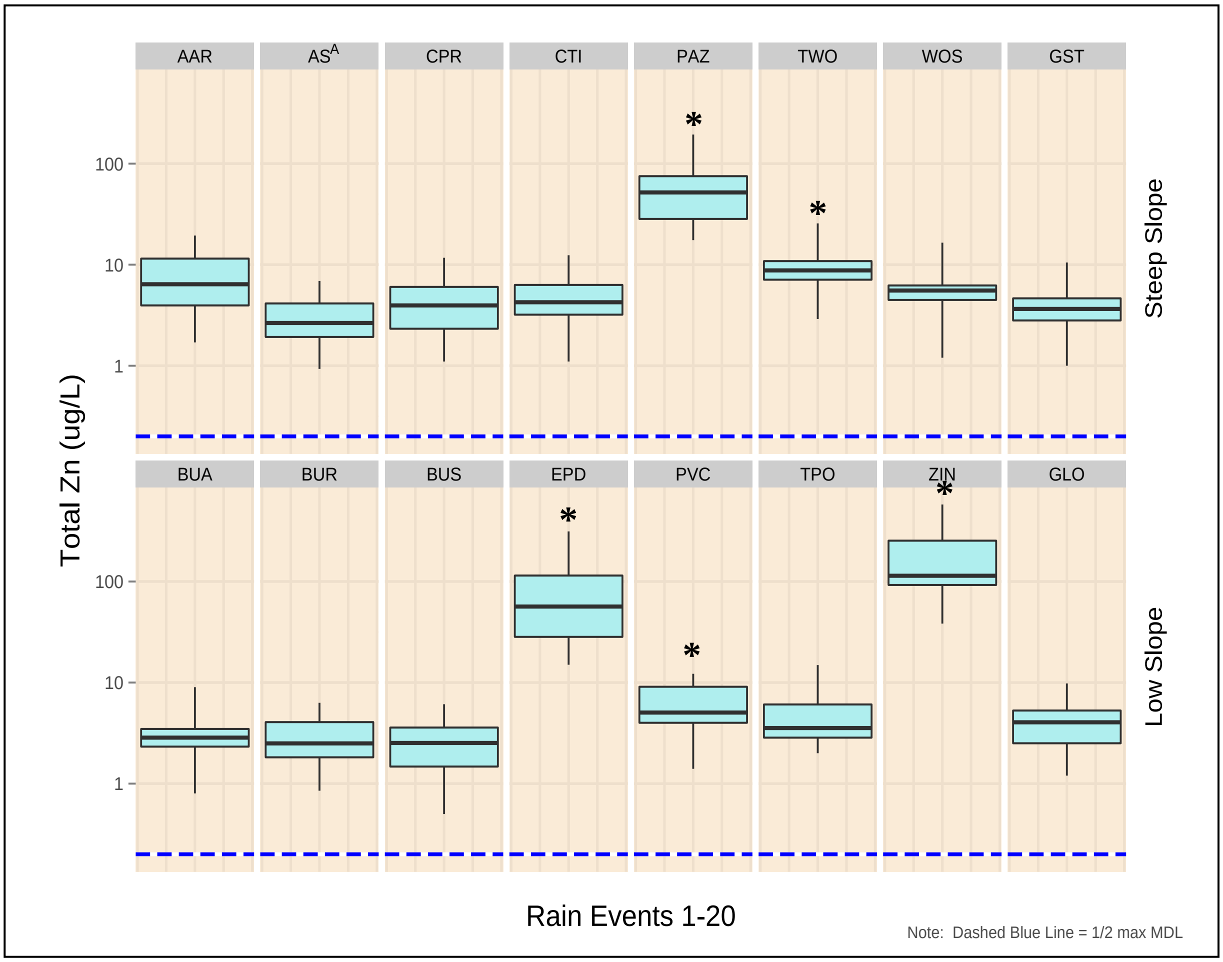


Figure 21. Box plots for total zinc concentrations across all panels.

* Runoff concentrations were statistically higher than those from the glass control panel.

Panel identification codes are defined in Table 1 on page 25.

The new EPDM roofing material (EPD) also released significantly higher concentrations of zinc than the low-slope glass control panel (GLO), although the median concentration was less than one-half of that for the Zincalume® panel. Zinc concentrations in runoff from the EPDM panel ranged from 15 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). The zinc catalyst serves as the likely source of zinc in the runoff.

Other panels that released significantly higher concentrations of total zinc to the runoff than the glass controls included:

- Painted galvanized metal (PAZ)
- Treated wood shake (TWO)
- PVC

Zinc concentrations in runoff from the painted galvanized steel panel (PAZ) ranged between 18 and 194 ug/L of zinc. The unpainted, galvanized edge of the roofing material may be the source of the zinc in the runoff. While the painted fasteners showed no signs of degradation, they may also have made a minor contribution to the zinc concentrations in runoff from this panel.

Total zinc from the treated wood shake panel (TWO) ranged from 2.9 to 26 ug/L. Concentrations of total zinc in runoff from the PVC panel ranged from 1.4 to 12 ug/L.

Ecology calculated the median total zinc concentration by panel type for each of the two sampling rounds (Table 20), and used box plots to visually depict the differences (Figure 22).

Table 20. Comparisons of Rounds 1 and 2 median total zinc concentrations (ug/L).

Round	**Steep-Slope Panels**							
	AAR	**AS**[A]	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**	**GST**
Round 1	**11**	**4.4**	**5.7**	**4.2**	**27**	**11**	**6.0**	**3.9**
Round 2	**3.9**	**2.2**	**2.4**	**4.8**	**63**	**7.1**	**5.0**	**3.6**
Significant Diff.	*				[a]	*	*	
Round	**Low-Slope Panels**							
	BUA	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
Round 1	**3.0**	**3.1**	**3.8**	**104**	**6.6**	**3.5**	**119**	**3.9**
Round 2	**2.7**	**2.3**	**1.5**	**27**	**4.2**	**3.8**	**110**	**4.1**
Significant Diff.				*	*			

* Yellow shading means a statistically lower concentration of total zinc released in Round 2.
[a] Yellow shading means a statistically higher concentration of total zinc released in Round 2.
Bold indicates analyte detected at or above the MDL.
Gray shading indicates glass control panels.
Panel identification codes are defined in Table 1 on page 25.

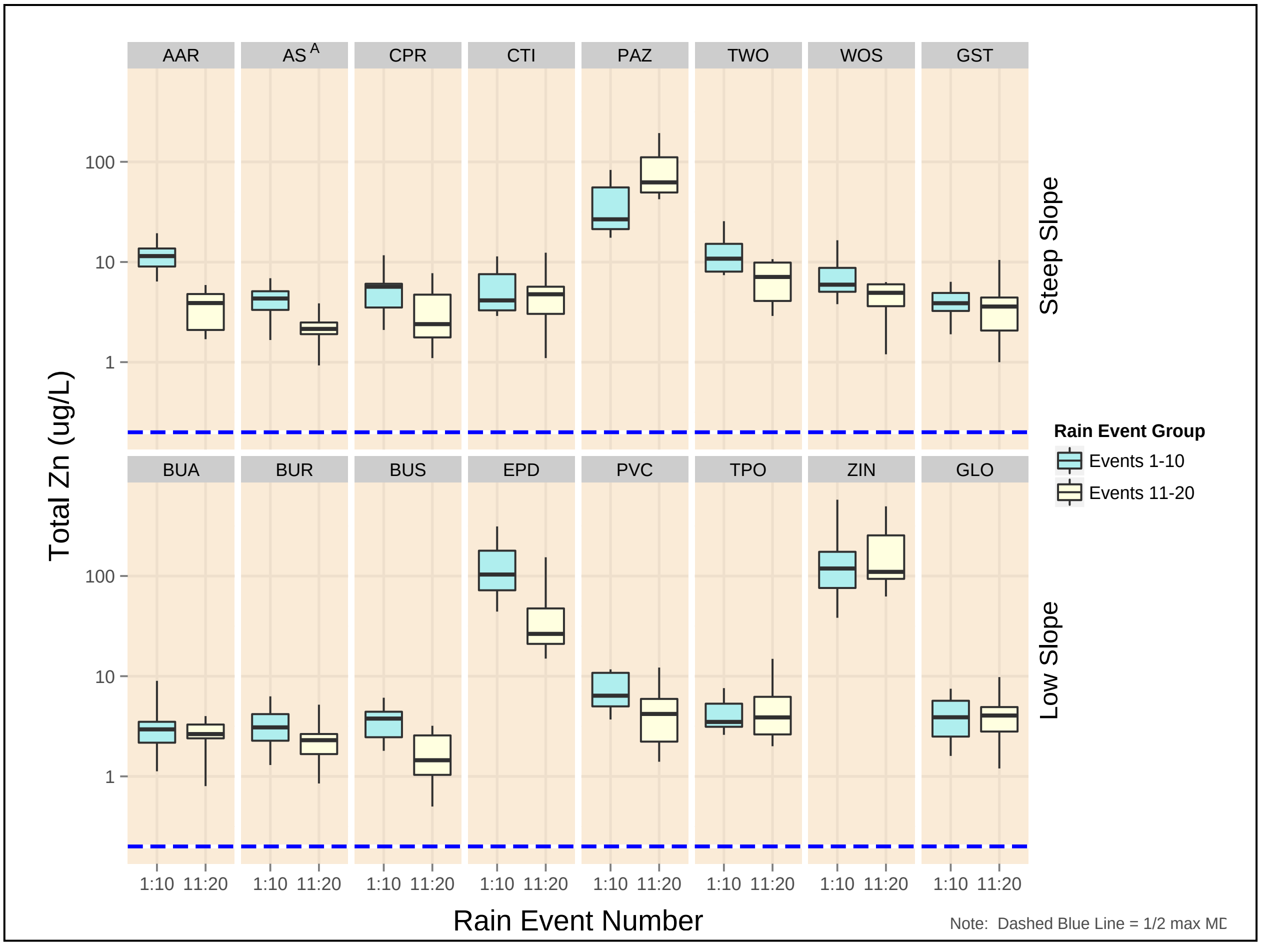


Figure 22. Box plots comparing total zinc concentrations from rain events 1-10 to rain events 11-20.

Panel identification codes are defined in Table 1 on page 25.

The Mann Whitney analysis comparing runoff concentrations between the two rounds found significantly lower concentrations (at $\alpha = 0.05$) of total zinc in runoff during Round 2 than during Round 1 for each of the following panels:

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

By contrast, the painted galvanized metal panel (PAZ) released significantly higher concentrations of zinc in Round 2 than in Round 1. Neither Ecology nor the RTF had a definitive explanation for this increase.

Impacts of Precipitation, Intensity, and Other Factors on Metals Concentrations

Ecology evaluated potential pair-wise relationships between metals concentration and each of the following parameters to determine whether significant correlations existed across roofing materials and metals:

- Precipitation amount
- Average, effective, and peak intensities of precipitation
- Length of the antecedent dry period
- Duration of rain event

Correlations between Metals Concentration and Precipitation

Ecology evaluated for statistically significant correlations using the Kendall's Tau non-parametric statistic. The test uses a ranking procedure to assess the "strength of a monotonic relationship between two variables" (Helsel and Hirsch, 2002). The Tau statistic depends only on the ranks of the data rather than on their values. The test is well-suited for skewed data, such as the runoff data from this project.

The Tau statistic is generally lower in value than traditional correlations coefficients (e.g., r) for linear associations of the same strength. Lower values do not indicate that the Tau statistic is less sensitive; rather it has a different scale. Ecology calculated the Tau statistic to determine whether the relationships were statistically significant at $\alpha = 0.05$. Differences existed in the rain event conditions between Round 1 and Round 2 (total amount of precipitation and average intensity were generally higher in Round 1, while the antecedent dry periods were longer in Round 2). Ecology also identified differences in metals concentrations between the two rounds. Thus, Ecology evaluated relationships for each round independently. Tables provide the Tau values for significant correlations, and figures depict representative examples graphically.

In assessing the relationship between the amount of precipitation in a rain event and the concentration of a metal in runoff from each of the roofing panels, Ecology staff generally identified relationships similar to those identified in the literature. Chang and Crowley (1993) noted a negative correlation between rainfall and zinc and lead concentration in runoff from several roofing types. Odnevall Wallinder and Leygraf (2001) demonstrated that copper in runoff was an inverse function of the amount of precipitation. He et al. (2001) also reported decreasing concentrations of copper and zinc with increasing precipitation amounts in runoff from copper and zinc roofing materials. These studies found that the relationships between concentration and amount of precipitation were prominent. Many authors have recognized such correlations as a function of the first-flush effect delivering higher concentrations of contaminants. RTF members postulated that higher rain falls could increase roofing material weathering and thereby result in lower concentrations released over time (RTF, pers. comm., 2014)

Table 21 lists the Tau values for inverse correlations between metals concentration and precipitation amount identified in this study. Negative Tau values indicate an inverse relationship—as the amount of precipitation increased, the concentration in runoff decreased. While Tau values were calculated for all comparisons, only concentrations differentiable from glass controls are the primary focus of further discussion. Table 21 highlights (green shading) 30 comparisons where the concentrations in runoff from the roofing panel were significantly higher than concentrations from the glass control panel.

Table 21. Significant Kendall's Tau values for correlations between total metal concentrations and precipitation by round and panel type.

	Steep-Slope Panels													
	AAR		**AS^A**		**CPR**		**CTI**		**PAZ**		**TWO**		**WOS**	
Round	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Arsenic	NS	NS	-0.51	-0.64	-0.42	NS	-0.60	-0.42	NS	NS	-0.44	-0.56	-0.56	-0.56
Cadmium	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	-0.64	NS	NS	NS
Copper	-0.67	-0.72	NS	-0.51	-0.58	-0.56	NS	NS	NS	NS	-0.53	-0.56	NS	NS
Lead	NS	NS	NS	NS	NS	NS	NS	NS	-0.58	NS	NS	NS	NS	-0.42
Zinc	-0.64	NS	NS	NS	NS	NS	NS	NS	-0.64	-0.56	-0.71	-0.42	-0.71	NS
	Low-Slope Panels													
	BUA		**BUR**		**BUS**		**EPD**		**PVC**		**TPO**		**ZIN**	
Round	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Arsenic	-0.53	-0.49	-0.69	-0.53	-0.67	NS	-0.51	NS	-0.71	-0.58	-0.73	-0.42	-0.42	-0.42
Cadmium	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Copper	NS	-0.47	NS	NS	NS	-0.60	-0.53	NS	NS	NS	NS	NS	-0.58	NS
Lead	NS	NS	NS	NS		NS	NS	NS	-0.49	NS	NS	NS	NS	NS
Zinc	NS	NS	NS	NS	NS	NS	-0.82	NS	NS	NS	NS	NS	-0.67	-0.47

NS: Inverse correlation was not significant at α = 0.05.
Green shading indicates runoff concentrations from the roofing panel were significantly higher than from the glass control for that round.
Panel identification codes are defined in Table 1 on page 25.

Ecology found that 24 of the 30 comparisons, or 80%, showed a significant inverse correlation. Figure 23 graphically depicts examples of the significant inverse correlations between concentration and precipitation for either Round 1 or Round 2. Ecology also found significant inverse correlations between arsenic concentrations and precipitation for eight of the panels, even though these concentrations were not statistically different from the glass control panels. Dry deposition of arsenic may be the source, and with greater rainfall the runoff becomes more dilute.

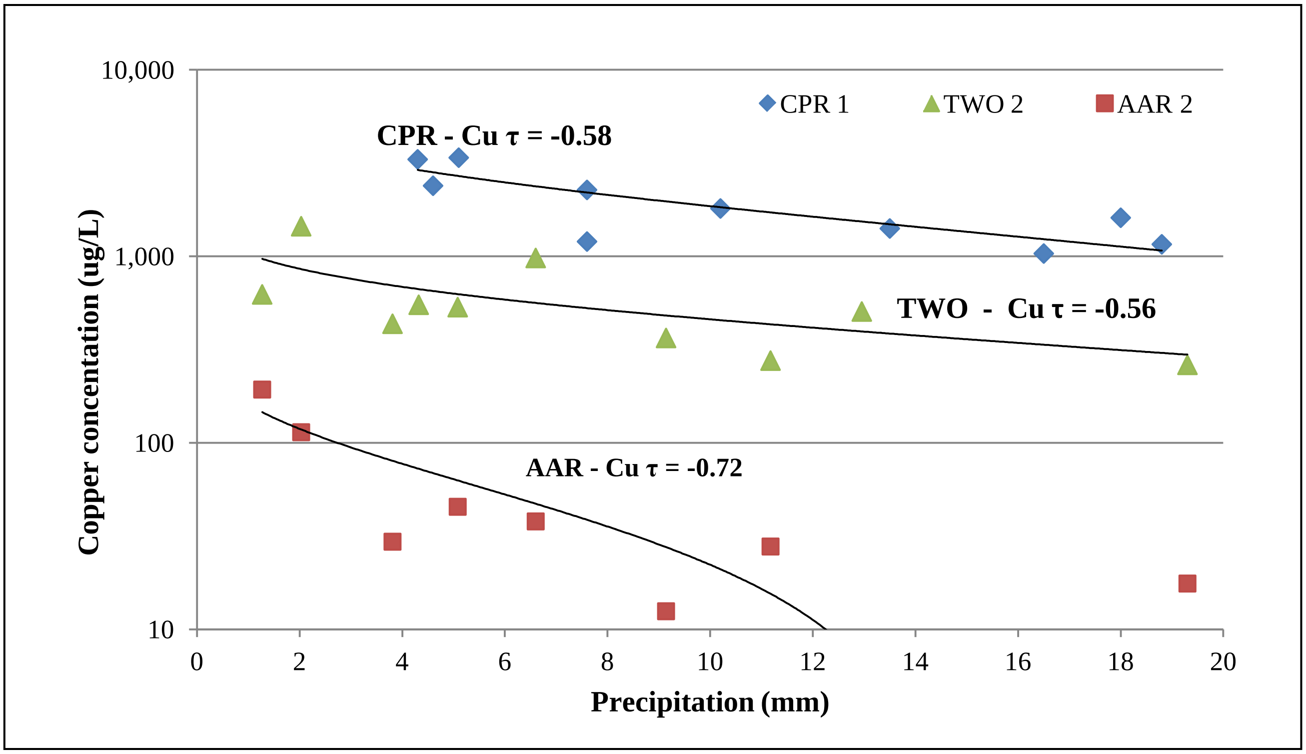


Figure 23. Examples of significant correlations between runoff metals concentrations and total precipitation.

Panel identification codes are defined in Table 1 on page 25.
Number associated with the panel identification code in the legend reflects monitoring Round (1 or 2).

Correlations between Metals Concentration and Rain Intensity

Ecology also used Kendall's Tau test to identify significant inverse correlations between concentration and average, peak, and effective rain intensity[6]. Effective intensity should serve as a more realistic measure in the Pacific Northwest, where rain frequently falls for discontinuous periods of drizzle and heavier rain. One would hypothesize that effective intensity should represent actual conditions experienced by the roofing panels.

However, Ecology found that the peak intensity (measured as highest rainfall in a 15-minute interval during a sampling event) was more often significantly correlated with metals concentrations than was either average or effective intensity. For all three of these measures, an inverse correlation exists—the lower the rain intensity, the higher the metals concentration. Table 22 presents the Tau values for correlations between concentrations and peak intensities. Table 22 also highlights (green shading) 30 comparisons where the concentrations in runoff from the roofing panel were significantly higher than those from the glass control panel. While Tau values were calculated for all comparisons, only concentrations differentiable from glass controls are the primary focus of further discussion.

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[6] Ecology staff defined *effective rain intensity* as the average of the 15-minute intervals during an event in which the tipping bucket rain gage recorded an amount.

Table 22. Significant Kendall's Tau values for correlations between total metals concentrations and peak rain intensity (in mm/15 min) by round and panel type.

	Steep-Slope Panels													
	AAR		**AS^A^**		**CPR**		**CTI**		**PAZ**		**TWO**		**WOS**	
Round	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Arsenic	NS	-0.53	NS	-0.48	NS	NS	-0.6	NS	NS	-0.49	-0.56	-0.47	NS	-0.47
Cadmium	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	-0.56	NS	NS	NS
Copper	NS	-0.79	NS	-0.44	-0.56	-0.53	NS	NS	NS	NS	-0.46	NS	NS	NS
Lead	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	-0.42
Zinc	-0.44	NS	NS	NS	NS	NS	NS	-0.44	-0.53	-0.48	-0.51	-0.42	-0.51	NS
	Slope Panels													
	BUA		**BUR**		**BUS**		**EPD**		**PVC**		**TPO**		**ZIN**	
Round	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Arsenic	NS	-0.44	-0.62	-0.42	NS	NS	-0.48	NS	-0.42	-0.49	-0.51	-0.47	NS	NS
Cadmium	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Copper	NS	-0.42	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Lead	NS	NS	NS	NS	NS	-0.44	NS	NS	NS	NS	NS	NS	NS	-0.46
Zinc	NS	NS	NS	NS	NS	NS	-0.56	NS	NS	NS	NS	NS	NS	NS

NS: Inverse correlation was not significant at $\alpha = 0.05$.
Green shading indicates runoff concentrations from the roofing panel were significantly higher than from the glass control for that round.
Panel identification codes are defined in Table 1 on page 25.

Of the possible 30 inverse correlations, 66% (or 20) were significant. Of these significant inverse correlations, most, but not all, occurred where metals concentrations were elevated. Ecology found 6 associated with the treated wood shake panel (TWO). Figure 24 depicts example correlations between total metals concentrations and peak rain intensity.

Even though concentrations in runoff from some panels were not statistically different from the glass control panels, runoff from seven panels showed significant inverse correlations between arsenic concentrations and peak rain intensities. Again, dry deposition of arsenic may be washed off more quickly and diluted faster with greater rainfall intensity.

These correlations were similar to the findings of He et al. (2001) who specifically assessed the impacts of intensity in the laboratory on copper and zinc roofing materials. Because this was a laboratory study, the effective, peak, and average intensities were controlled and the same for an event. They reported an inverse relationship between intensity and concentration; at low intensity (drizzle of 1 mm/hr), copper and zinc concentrations were highest.

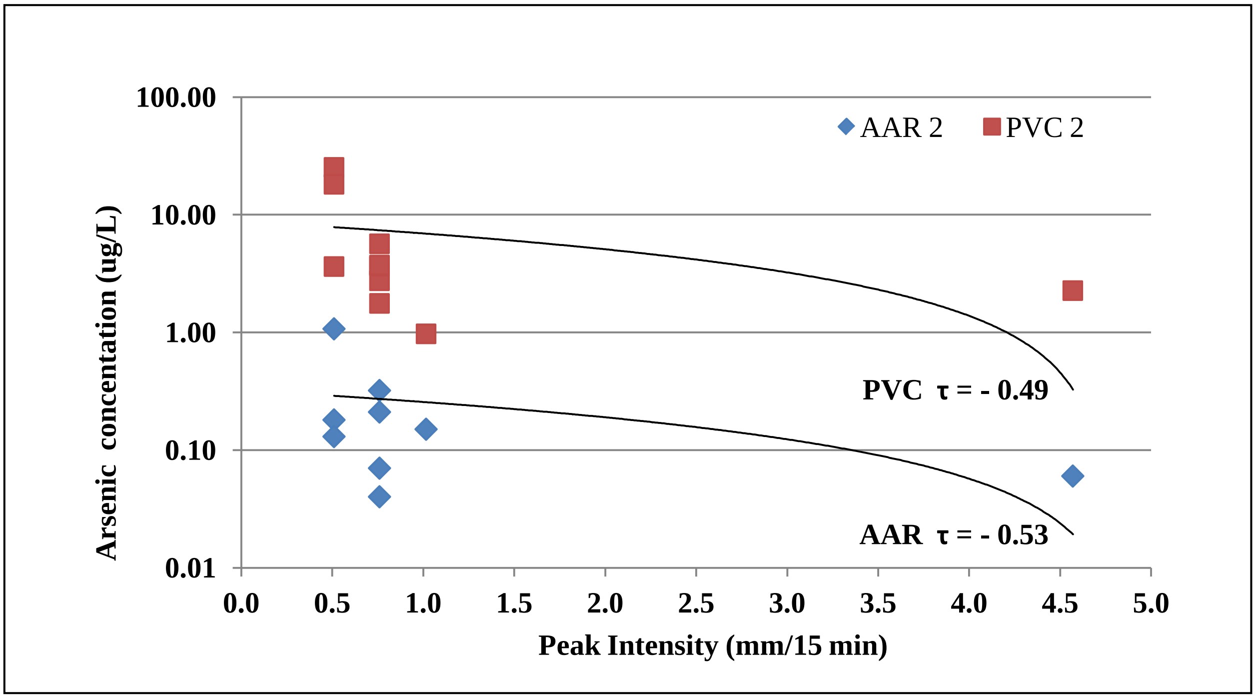

Figure 24. Examples of significant correlations between runoff metals concentrations and peak rain intensity.

Panel identification codes are defined in Table 1 on page 25.

Number associated with the panel identification code in the legend reflects monitoring Round (1 or 2).

Correlations between Metals Concentration and Antecedent Dry Period

Ecology evaluated the relationships between the length of the antecedent dry period and the concentration of total metal using the Kendall's Tau statistic. For this analysis, Ecology eliminated the data in which there was no antecedent dry period. (The data from rain events 3 through 6 were not included because collection of samples began after the onset of precipitation.) Ecology found significant positive linear relationships between concentration and antecedent dry period. As the length of the antecedent dry period increased, the concentration of total metals also increased. Table 23 highlights (green shading) 30 comparisons where metals concentrations in runoff from the roofing panel were significantly higher than those from the glass control.

Table 23. Significant Kendall's Tau values for correlations between total metals concentrations and length of antecedent dry period by round and panel type.

	Steep-Slope Panels													
	AAR		**AS^A**		**CPR**		**CTI**		**PAZ**		**TWO**		**WOS**	
Round	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Arsenic	🟩 NS	NS	NS	NS	0.73	NS	🟩 NS	🟩 0.44	NS	0.47	🟩 NS	🟩 NS	🟩 NS	🟩 0.44
Cadmium	NS	NS	NS	NS	🟩 NS	NS	NS	NS	NS	NS	🟩 NS	🟩 NS	NS	NS
Copper	🟩 NS	🟩 NS	🟩 NS	🟩 NS	🟩 NS	🟩 0.44	NS	NS	NS	0.51	🟩 NS	🟩 NS	NS	NS
Lead	NS	NS	NS	NS	NS	0.49	NS	NS	NS	NS	NS	NS	NS	NS
Zinc	🟩 NS	0.44	NS	NS	NS	0.58	NS	NS	🟩 NS	🟩 0.47	🟩 NS	🟩 NS	🟩 NS	NS

	Low-Slope Panels													
	BUA		**BUR**		**BUS**		**EPD**		**PVC**		**TPO**		**ZIN**	
Round	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Arsenic	NS	0.44	NS	0.51	NS	0.53	NS	NS	🟩 NS	🟩 NS	NS	NS	NS	NS
Cadmium	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Copper	NS	NS	NS	NS	NS	0.49	NS	0.62	NS	0.58	NS	0.62	NS	0.80
Lead	NS	0.53	NS	NS	NS	NS	NS	0.51	NS	NS	NS	NS	NS	0.69
Zinc	NS	-0.42	NS	NS	NS	NS	🟩 NS	🟩 0.44	0.80	0.53	NS	NS	🟩 NS	🟩 0.44

NS: Correlation not significant at $\alpha = 0.05$.
Green shading indicates comparisons in concentrations from the roofing panel were significantly higher than from the glass control for that round.
Panel identification codes are defined in Table 1 on page 25.

Positive correlations between concentration and antecedent dry period were less prevalent than for the other two rain parameters. Of the possible 30 positive correlations, 20% were significant. Each of the 6 significant positive correlations identified occurred in the Round 2 monitoring. This may be a function of the fact that Round 2 had a much broader range of antecedent dry periods (from 21.5 to 141.25 hours). By contrast, Round 1 antecedent dry periods ranged from 0.25 to 66.5 hours. Figure 25 provides several examples from Round 2 data for copper.

Higher concentrations have been observed with longer antecedent dry periods. The higher concentrations are usually associated with aerial deposition. Yaziz et al. (1989) reported a positive relationship between the length of the dry period and the concentrations of zinc, lead, and conventional contaminants. Similarly, Thomas and Greene (1993) reported positive correlations between the length of the dry period and suspended solids, turbidity, and lead concentrations. With longer dry periods, the correlations become more pronounced. The length of the dry period that Thomas and Greene recorded stretched to twice as long as the conditions in this study.

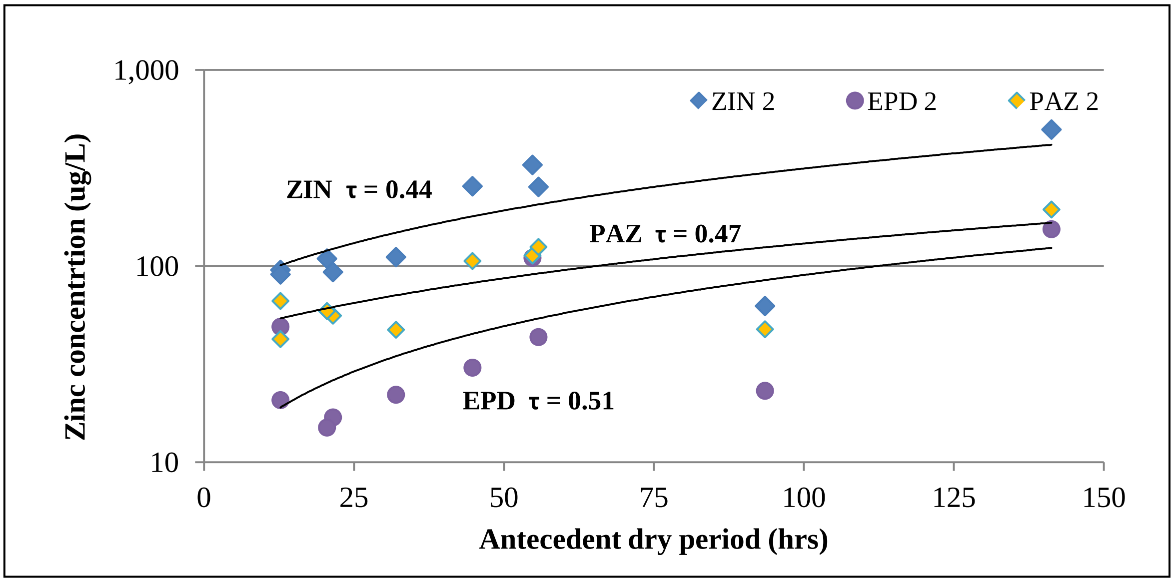

Figure 25. Examples of significant correlations between runoff metals concentrations and the length of the antecedent dry period.

Panel identification codes are defined in Table 1 on page 25.
Number associated with the panel identification code in the legend reflects monitoring Round (1 or 2).

Correlations between Metals Concentration and Rain Event Duration

Literature indicates a correlation between rain event duration and metals concentration. Ecology had already identified a significant inverse correlation between precipitation amount and concentration. Ecology identified a correlation between duration and precipitation amount and assumed the correlation between duration and metals concentration would be similar to those between precipitation and metals concentration.

Using Correlations to Predict Rain Event Concentrations

Based on these relationships, one might anticipate rain event 11 – with the longest antecedent dry period, the second lowest amount of rain, and the lowest rain intensity – to have the highest metals concentrations released in runoff. Because the concentrations in Round 2 generally differed significantly from those in Round 1, Ecology compared only those concentrations across rain events within Round 2. Rain event 11 produced the highest concentrations of metals from the following roofing material types:

- Arsenic in runoff from all roofing materials and the glass control panels.
- Copper in runoff from all roofing materials and the glass control panels, except from the asphalt shingle panel with AR (AAR) and concrete tile (CTI) panels.
- Lead in runoff from five of the roofing materials and the steep glass control panel. Lead concentrations in runoff from the modified built-up roofing with APP (BUA) and the modified built-up roofing with SBS (BUS) panels were tied for highest metals concentration measured.
- Zinc in runoff from one-half of the roofing materials and from both glass control panels.

Ecology also evaluated metals concentrations from rain event 7, anticipating the lowest concentrations based on the predictive relationships discussed previously. Rain event 7 produced the second highest amount of precipitation, had a moderate antecedent dry period length, and had the third highest rain intensity. However, because rain event 7 was not the most extreme for the parameters assessed, the relationships were less straight forward. Thus while one might predict that rain event 7 would result in low metals concentrations, Ecology found no consistent pattern.

Total Metals Released to Runoff

Ecology calculated the total metals released in runoff from the panels (sometimes termed *mass load*) only for roofing materials which had significantly higher concentrations in runoff than in runoff from the glass control panel. Ecology calculated these by multiplying the concentrations by the volume recovered from each rain event, dividing by the projected surface area. Then, Ecology subtracted the mass released from the glass control from that released from the roofing material for each event. Table 24 lists the maximum and minimum values across all rain events, as well as the median values across all events and across events 1-10 (Round 1), and events 11-20 (Round 2). Table 24 does not include release rates for those roofing materials that did not differ significantly from the glass controls.

Release rates generally differed between Rounds 1 and 2, paralleling the concentrations. Of these, only the painted galvanized metal panel (PAZ) released significantly higher rates of zinc in Round 2 than in Round 1.

The ranges are presented in Table 24 because of the variability of both the metals concentrations and the percent recovery for the volumes collected. The relationship between concentration and amount of precipitation, as discussed previously, also has an impact on the released metals calculations. The calculated release rates in Table 24 should not necessarily be applied directly to other studies for at least three reasons:

- The release rates changed with the aging of the roofing materials, even in the short one-year period from the beginning of the study. Extrapolation to roofing materials of various ages may, therefore, not be accurate.
- As described in the previous section, the relationships between metals concentration and amount of precipitation, its intensity, and the antecedent dry period vary. Using an average or median value for a release rate to calculate whole basin releases may not accurately represent the conditions within the basin.
- The roofing panels used in this study represented a run-length of less than 3 meters, much less than on many 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 loads of metals than those presented in Table 24. Roofs do not tend to have standardized run lengths.

Table 24. Maximum, minimum, and median total metals released (ug/m^2) by round and panel type.*

Metal	Statistic	Steep-Slope Panels							Low-Slope Panels		
		AAR	AS[A]	CPR	CTI	PAZ	TWO	WOS	EPD	PVC	ZIN
Arsenic	Maximum	14			5.1		33,632	4.7		757	
	Minimum	<G			0.8		1,157	<G		14	
	Median 1-20	1.1			2.4		10,539	0.5		162	
	Median 1-10	1.8			2.7		17,507	0.9		394	
	Median 11-20	0.5			2.0		5,393	0.2		24	
Cadmium	Maximum						2.5				
	Minimum						0.1				
	Median 1-20						0.9				
	Median 1-10						1.3				
	Median 11-20						0.5				
Copper	Maximum	678	65	28,976							
	Minimum	<G	<G	4,756							
	Median 1-20	258	5.8	18,226							
	Median 1-10	389	40	18,948							
	Median 11-20	220	3	13,187							
Lead	Maximum				27						
	Minimum				<G						
	Median 1-20				1.3						
	Median 1-10				1.0						
	Median 11-20				1.6						
Zinc	Maximum					816	150		1,929		3,142
	Minimum					144	<G		58		369
	Median 1-20					323	41		650		972
	Median 1-10					286	67		979		849
	Median 11-20					517	13		172		1,069

* Table includes release rates only for those panels with significantly higher release rates than the glass control panels.
[A] Average of three replicate asphalt shingle panels.
<G: Less than the glass control.
Panel identification codes are defined in Table 1 on page 25.

Total Metals Comparisons with the Puget Sound Toxics Assessment

Ecology calculated the median metals 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 calculated a median concentration for each metal by roofing material across the Round 2 rain events and subtracted the median glass control panel concentration (using either the steep-slope or low-slope control panels, as appropriate).

Subtraction of concentrations measured from the control panels is the same technique used by Clark (2010) and Chang et al. (2004). The concentrations of metals in runoff obtained for Round 2 by these calculations were then compared to release estimates within the Puget Sound basin from the Puget Sound Toxics Assessment (Ecology, 2011a). These comparisons are shown in Table 25 for similar roofs.

With one exception, the comparison reveals that concentrations used in the Puget Sound Toxics Assessment (Ecology, 2011a) ranged from 30% to three orders of magnitude higher. Only copper concentrations in runoff from the copper panel (CPR) were similar (similarity was determined as within 30% of one another and indicated by yellow shading in the table). 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.

Low metals concentrations released from the new roofing materials assessed in this study 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.
- Galvanized roofs generally release higher concentrations of zinc than the Zincalume® material evaluated in this study (Heijerick et al., 2002). Existing galvanized metal roofs in the Puget Sound region could contribute higher concentrations (and mass) than concentrations measured from the Zincalume® panel (ZIN) in this study.
- Low metals concentrations obtained in this study from panels at specific slopes may not be directly applicable to roofs of the same material installed at a different slope.
- The length of the pilot roofing 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.

Because runoff concentrations depend on a number of factors – including the specific roofing materials and components, age of the materials, length of the roof, angle of roof installation, and the climatic conditions described above – application of literature runoff concentrations to Puget Sound basin-wide releases should be undertaken cautiously.

Table 25. Comparisons of concentrations of metals (ug/L) used to estimate releases in Puget Sound to concentrations in Round 2 of this study.

Roof Type	Arsenic	Cadmium	Copper	Lead	Zinc
	ug/L				
PSTA Study					
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
Roofing Assessment					
Asphalt shingle with AR	0.1	<0.01	29	<0.01	<0.1
Asphalt shingle	0.03	<0.01	0.4	<0.01	<0.1
Metal (PAZ)	0.01	<0.01	<0.01	0.01	61
Metal (ZIN)	<0.02	<0.01	<0.01	0.01	108
Copper	<0.02	<0.01	1,985	0.1	<0.1
Concrete Tile	0.3	<0.01	0.2	0.2	3.0
Treated Wood Shake	932	0.09	519	<0.01	3.0
Wood Shingle	0.05	<0.01	0	<0.01	0.7
Built-up and modified built-up roofing (BUR, BUA, BUS)	≤0.02	<0.01	<0.01	<0.01	<0.1
EPDM	<0.02	<0.01	<0.01	<0.01	23
PVC	3.6	<0.01	<0.01	<0.01	3.0
TPO	<0.02	<0.01	<0.01	<0.01	0.5

[a] Ecology (2011a) values were based on a misreading by Clark (2008) from a chart reported by Tobiason (2004). The re-calculated value is 22 ug/L, based on the average of the values reported by Good (1993) and average values by Tobiason (2004).

PSTA: Puget Sound Toxics Assessment (Ecology, 2011a).

Panel identification codes are defined in Table 1 on page 25.

Yellow-highlighted, cells indicate similarities with this study.

Total Metals Comparisons with Literature Values

To compare data from this study with the literature, Ecology assessed the ranges of metals concentrations across all 20 rain events. Because some of the metals could have originated from sources other than the roofing materials (e.g., from aerial deposition), Ecology determined the concentration for each metal by roofing material for each rain event, subtracting the glass control panel concentration (using either steep-slope or low-slope panels, as appropriate) for that event. Ecology calculated metals concentrations for comparison with the literature values.

Subtraction of metals concentrations measured from the control panels is the same technique used by Clark (2010) and Chang et al. (2004). As shown in Table 26, some of the literature calculations resulted in negative values for some metals concentrations, indicating that those roofing materials were not a likely source for that metal. For the results of this study, a less than the detection limit was used rather than negative numbers.

The median concentrations in Table 26 were compared to other literature studies 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, 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 Table 26, green-highlighted ranges represent median values from the current study. Yellow-highlighted concentrations from the literature represent concentrations within the range of those found in this study. For the purposes of these comparisons, values within 30% of one another are considered “within the range.” In the table, the *Notes* column identifies whether authors studied full-scale roof systems or panels.

Table 26. Comparisons of metals concentrations (ug/L) from roofing materials in the literature to median metals concentrations measured in this study.

Total metals concentration from the literature represent post first-flush means, medians, or mean concentrations. Concentrations from this study represent 20 rain event medians minus the glass control panel medians.

Roof Type	Location	Arsenic	Cadmium	Copper	Lead	Zinc	Notes	Author
		ug/L						
Asphalt Shingle Roofs								
AS^{A}	WA	0.03	0.0	1.2	-0.07	-1.2	P	This study
AAR	WA	0.16	0.0	30	-0.09	3.0	P	This study
Asphalt shingles	PA	0.3	-0.1	-55	-0.6	0.0	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)
Galvalume®, Zincalume®, etc. Roofs								
Zincalume®	WA	0.0	0.0	-0.01	0.0	111	P	This study
Galvalume® (55% aluminum, zinc coated steel)	WA			355		2,890	RS	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® (Al coated)	Sweden					1,600	P	Heijerick et al. (2002)
Pre-painted Galvanized Roofs								
PAZ	WA	0.01	0.0	0.06	0.01	49	P	This study
Prepainted Zincalume®	WA			1.3		146	S	Herrera (2011)
Prepainted galvanized steel	Sweden					160	P	Heijerick et al. (2002)
Painted steel	Sweden					2,100	P	Persson & Kucera (2001)
Prepainted galvanized steel, with zinc coating and polyester top coat	France		ND	2.9	0.5	31	P	Robert-Sainte et al. (2009)

Roof Type	Location	Arsenic	Cadmium	Copper	Lead	Zinc	Notes	Author
		ug/L						
Copper Roofs								
CPR	WA	0.0	0.0	1,905	0.11	0.3	P	This study
Copper	Sweden			3,575			P	Persson & Kucera (2001)
Copper	Maryland			980			P	LaBarre et al. (2014)
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)
Wood and Treated Wood Roofs								
WOS	WA	0.09	0.0	0.28	-0.10	1.40	P	This study
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			29	45	16,317	P	Chang et al. (2004)
TWO	WA	1,385	0.10	825	-0.08	4.0	P	This study
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)
Concrete Tile Roofs								
CTI	WA	0.28	0.0	0.16	0.11	1.3	P	This study
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)
Built-Up Roofs and Materials								
BUR	WA	0.01	0.0	0.01	-0.12	-1.0	P	This study
BUA	WA	0.0	0.0	-0.10	-0.13	-1.1	P	This study
BUS	WA	0.04	0.0	-0.01	-0.13	-1.2	P	This study
BUR with white APP cap sheet*	TX	<0.29	<0.10	1.3	0.6	46	P	Mendez et al. (2010)

Roof Type	Location	Arsenic	Cadmium	Copper	Lead	Zinc	Notes	Author
		ug/L						
Rock and tar (built-up)*	TX				12	4,880	RS	Chang & Crowley (1993)
Roofing felt	PA	0.3	0.3	-74	1.1	0.0	P	Clark (2010)
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)
Single Ply Roofs								
EPDM	WA	-0.03	0.0	-0.11	-0.07	54	P	This study
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	20.0	0.00	-0.06	-0.02	1.9	P	This study
Corrugated PVC	PA	0.1	-0.3	0.0	0.1	ND	P	Clark (2010)
TPO	WA	-0.01	0.0	0.0	-0.03	0.8	P	This study
Cool	TX	<0.29	<0.10	1.3	0.6	46	P	Mendez et al. (2010)
Polyester	Switz.			217	4.9	27	RS, cu	Zorbrist et al. (2000)

^{A} Average of three replicate asphalt shingle roofs.

* Aerial deposition not subtracted.

ND: Not detected.

Green-highlighted cells indicate median values from this study.

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

Notes column: RS: full-scale installed roofing system; P = roofing panels; cu = copper gutter; g = galvanized gutter.

Panel identification codes are defined in Table 1 on page 25.

Asphalt Shingle Roofs

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

- The Clark (2010) study evaluated shingles with AR. She reported total metals concentrations were within the ranges of the low concentrations for cadmium, lead, and zinc in runoff from both the asphalt shingle with AR (AAR) and the asphalt shingle (AS^A) roofing panels in this study. Neither of these roofing materials was similar to the results Clark obtained for copper. Clark's results may have been affected by large amounts of atmospheric copper deposition.
- The arsenic, cadmium, and copper concentrations in runoff from the asphalt shingle panel with AR (AAR) were similar to metals concentrations reported by Mendez et al. (2010), although the zinc concentrations in the Mendez study were higher.
- Copper concentrations in runoff from asphalt shingle panels with AR (AAR) in this study were also similar to runoff from the panel in the Chang et al. (2004) study. Chang's concentrations for zinc were much higher than those measured in the present study, for the reasons mentioned previously.
- Zinc and lead concentrations in runoff from asphalt shingle roofing systems studied by Steuer et al. (1997) were higher than in this study. Their higher concentrations were likely due to monitoring complete roofing systems with flow-through gutters and downspouts. They also studied full-scale roofs of varying ages.

Galvalume® and Zincalume® Roofs

Table 26 provides literatures values for Galvalume® and Zincalume® roofing systems and panels. Zincalume® is a trade name for a Galvalume®-type product. Few similarities are noted with the results of this study. Zinc, arsenic, and cadmium concentrations measured in runoff from the Mendez (2010) study showed similarities with this study.

The median zinc concentration from the Zincalume® roofing panel (ZIN) in this study (106 ug/L) was more than an order of magnitude lower than those reported in the studies of Heijerick et al. (2002) and Tobiason (2004). The Galvalume® and Galfan® reported by Heijerick et al. (2002) may reflect a different manufacturing process in Sweden, different precipitation amounts, and/or panel size, or slope. The higher concentrations measured by Tobiason in Washington State may reflect monitoring of runoff from an aged, complete roofing system with a substantially longer run length.

Zinc concentrations in runoff in this study were also approximately one-tenth of those for galvanized roofing systems surfaces reported by Gromaire et al. (2002), Robert-Sainte et al. (2009), Heijerick et al. (2002), Good (1993), and Chang et al. (2004). The European results (Gromaire et al., Robert-Sainte et al., and Heijerick et al.) may reflect a substantially different manufacturing process. The higher results obtained by Good, while in Washington State, are likely a result of first-flush sampling.

Zinc concentrations in runoff are strongly influenced by amount of precipitation, corrosivity of the rain, and roofing panel size and orientation. Therefore, the zinc concentration from Zincalume® steel will vary considerably from site to site and test to test, in additional to temporal variation. However, the relative difference between different products in the same set of test conditions is likely to be consistent.

Pre-painted Galvanized Roofs

The literature generally reported higher concentrations of zinc in runoff from pre-painted metal roofs than in this study (Table 26). However, the zinc concentrations reported by Robert-Sainte et al. (2009) study were only slightly lower than those measured in this study.

Although Taylor Associates (2004) investigated post-manufactured painting, their results merit noting. They reported up to 87% reductions in the zinc concentrations released using a synthetic rain application. Their results were more than two times the results from this study. Differences could be attributable to longer, full-scale roof lengths, or to differences between the synthetic rain used and actual precipitation. The Tobiason et al. (2006) study, which was also conducted in Washington, found general reductions of approximately 37% in the total zinc released from a Galvalume® surface after painting and subsequent removal of gutter sediments. Except for their outlier values, the zinc concentrations in runoff from the post-manufactured painted Galvalume® surface hovered near the Industrial Stormwater General Permit benchmark of 117 ug/L, similar to results of the pre-painted galvanized panel (PAZ) in this study.

Copper Roofs

The copper roof panel (CPR) produced runoff concentration ranges similar to those reported by Pennington and Webster-Brown (2008) for eight-year-old roofs, as well as the aged copper roofs reported in Connecticut by Boulanger and Nikolaidis (2003). The higher copper concentrations reported by Persson and Kucera (2001) in Sweden (closer to the higher end of the concentration range in this study) may be attributed to the authors' evaluation of full-scale roof systems. The LaBarre et al. (2014) study of 10- by 20-foot copper panels showed a substantially lower average copper concentration of 980 ug/L in the roof runoff.

Treated and Untreated Wood Roofs

Table 26 shows very little similarity between literature values and the concentrations of total metals detected in the panel runoff in this study. This may be a result of generally very low concentrations of all the measured metals in the untreated wood panel (WOS).

The elevated zinc concentrations reported by Chang et al. (2004) likely reflect the galvanized gutters they used to collect the samples.

The 201 ug/L of zinc reported by Clark (2010) is surprising because she did not collect runoff in galvanized gutters. Comparison with Khan et al. (2006) (not in Table 26) and Clark (2010) showed similar results for zinc from the untreated plywood. The elevated zinc results Clark found in runoff from the cedar shake panel may reflect different soil chemistry for the trees used to produce the cedar shakes, or may reflect the lower pH of the rain (4.3) leading to greater zinc solubility.

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 found concentrations of cadmium and lead from pressure treated wood similar to those in runoff from the treated wood shake panel (TWO) in this study. 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 (TWO) were higher than the average of 600 ug/L cited by Khan et al. (2006) for CCA-treated deck materials (not in Table 26), but within the range they measured (up to 8,400 ug/L). Lebow et al. (2008) assessed leaching from CCA-treated lumber using simulated rain water. They reported copper results on the basis of load per millimeter of rain. When concentrations of copper released from the treated wood panel in Round 2 of this study are converted to those units, results are comparable (0.47 mg/m^2/mm) to the average values cited by Lebow et al.

Concrete Tile Roofs

The concrete tile roofing panel (CTI) in this study showed few similarities with concentrations of metals in runoff from tile roofs in the literature (Table 26). Only the low concentrations of arsenic and cadmium measured by Mendez et al. (2010) were similar to those measured in this study. Differences in copper and zinc in runoff from roofs and panels studied by Mendez, Yaziz et al. (1989) and Person and Kucera (2001) may be attributable to differences in concrete source materials or rain pH values.

Built-up Roofs

Literature results for runoff from various built-up roofing materials are not extensive. The three built-up and modified built-up roofing panels (BUR, BUA, and BUS) in this study resulted in low total metals concentrations in the runoff. The results of this study were not similar to the concentrations of zinc, 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 also used galvanized gutters and reported elevated zinc concentrations. Mendez et al. (2010) found similar concentrations of arsenic and cadmium in runoff from their panels, even though aerial deposition was not subtracted for their study.

Single-Ply Roofs

Single-ply roofing materials have not been as thoroughly reported in the literature. The Ondura® panel in the Clark (2010) study produced similar concentrations of zinc in runoff as the EPDM panel (EPD) in this study. Runoff from the Ondura® panel also resulted in similar, low concentrations of arsenic, copper, and cadmium.

Runoff from Clark's corrugated PVC control panel resulted in concentrations of cadmium, copper, and lead similar to this study. Noteworthy in this study was the elevated arsenic concentration in the PVC panel runoff, which was thought to be attributable to an added biocide (RTF, pers. comm., 2013).

Runoff from the TPO panel in this study showed similarities only to the low concentrations of arsenic and cadmium measured in runoff from the Mendez Cool roof panel.

Organic Compounds

PAHs

The specific PAH compounds detected and their concentrations continued to exhibit the spatial variability in the sampled rain events during Round 2 that was observed in Round 1. This variability likely relates to the heterogeneity of aerial deposition. Ecology calculated the sums of the detected PAH compounds for each roofing panel and each rain event. Appendix B presents the sums of the detected PAH concentrations for each panel and each rain event.

Ecology used the Wilcoxon signed-rank test to compare each roofing panel to its glass control panel to determine statistical differences between roofing panels and the applicable control panel. Only runoff from the EPDM panel (EPD) had significantly higher concentrations of PAHs than the low-slope glass control panel (GLO) at $\alpha = 0.05$ across all 20 rain events. This was entirely attributable to Round 1 sampling results. Whether or not this is a function of the roofing material or spatial variability in aerial deposition should be re-evaluated as the panel ages.

Ecology also found that significantly higher total PAH concentrations in runoff from the modified built-up roofing with SBS (BUS) panel than from either the built-up roofing panel (BUR) or the modified built-up roofing panel with APP (BUA). This was also predominantly attributable to the Round 1 sampling results. In fact, Ecology found that the modified built-up roofing with SBS (BUS) had significantly higher total PAH concentrations than the glass control panel (GLO) in Round 1. On the other hand, the low-slope glass control panel had significantly higher total PAH concentrations than either the built-up roofing panel (BUR) or the modified built-up roofing panel with APP (BUA) in Round 1. This would lead one to attribute these differences to significant spatial heterogeneity of aerial deposition of PAHs. These differences should continue to be evaluated as the roofing materials age.

Ecology calculated the median concentration for the sum of the detected PAHs by panel type for Rounds 1 and 2 separately. Table 27 displays those median, maximum, and minimum concentrations. Statistical analyses comparing Round 1 with Round 2 results were not performed because of the limited number of samples in Round 2. By way of observation, median concentrations of total detected PAHs in runoff from the panels tended to be higher in Round 2 than Round 1. This might be attributable to the fact that all of the events in Round 2 followed a period without any precipitation of at least six hours. The lower average ambient air temperatures during Round 2 may have triggered an increased frequency of wood stove burning and associated PAH release in the vicinity.

The data suggest that the new roofing materials assessed in this study generally do not release PAHs to runoff. As roofing materials age, this trend needs to be assessed.

Table 27. Median, maximum, and minimum concentrations of the sum of detected PAHs (ug/L) in runoff by panel and sampling round.

Round 1	**Steep-Slope Panels**								**Low-Slope Panels**							
	AAR	**AS[A]**	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**	**GST**	**BUA**	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
Median	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
Max.	0.03	0.04	0.05	0.04	0.05	0.06	0.13	0.09	0.04	0.04	0.13	0.10	0.04	0.06	0.05	0.07
Min.	0.01	0.01	0.01	0.02	0.02	0.02	0.01	ND	ND	ND	0.03	0.04	ND	ND	0.03	ND
Round 2	**Steep-Slope Panels**								**Low-Slope Panels**							
	AAR	**AS[A]**	**CPR**	**CTI**	**PAZ**	**TWO**	**WOS**	**GST**	**BUA**	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
Median	0.10	0.12	0.10	0.09	0.11	0.07	0.20	0.10	0.08	0.10	0.09	0.07	0.05	0.07	0.06	0.08
Max.	0.10	0.12	0.16	0.22	0.15	0.12	0.32	0.17	0.10	0.10	0.10	0.16	0.11	0.19	0.14	0.18
Min.	0.10	0.04	0.04	0.04	0.04	0.04	0.09	0.03	0.03	0.03	0.04	0.03	0.02	0.02	0.03	0.02

ND: No PAHs detected.
Shading indicates glass control panel.
Panel identification codes are defined in Table 1 on page 25.

Phthalates

Phthalates (plasticizers) were detected in runoff from the roofing panels only sporadically during both sampling rounds. Generally, concentrations of the six phthalate compounds monitored were low across all roofs. (See Appendix B for analytical results.) Table 8 in the *Results* section lists the specific phthalate compounds detected and the number of rain events in which each compound was detected. Noteworthy is the fact that none of the phthalates detected in runoff from a panel in Round 1 were detected in Round 2.

Ecology calculated the sums of the detected phthalates for each panel and each rain event (Appendix B). Ecology calculated the median values of the sum of the detected phthalate compounds (Table 28). The phthalates were not detected, or were only detected at concentrations slightly above the glass control panels, except for the treated wood shake panel (TWO) in Round 1. Measurable phthalates were detected in runoff from only the treated wood shake, EPDM, and TPO panels in Round 2. By Round 2, the phthalate concentrations in runoff had declined to undetectable or very low concentrations across all panels.

Table 28. Median concentration of the sum of the detected phthalates (ug/L) by panel for sampling Rounds 1 and 2.

Round	Steep-Slope Panels							
	AAR	AS^A	CPR	CTI	PAZ	TWO	WOS	GST
1	ND	0.43	0.57	ND	0.02	4.2	0.85	ND
2	ND	ND	ND	ND	ND	0.13	ND	ND
Round	**Low-Slope Panels**							
	BUA	**BUR**	**BUS**	**EPD**	**PVC**	**TPO**	**ZIN**	**GLO**
1	0.25	0.20	0.20	0.22	0.44	0.38	ND	0.48
2	ND	ND	ND	0.11	ND	0.12	ND	ND

ND: Not detected at the method detection limit (MDL).
Shading indicates glass control panels.
Panel identification codes are defined in Table 1 on page 25.

The treated wood shake panel (TWO) had concentrations of detected phthalates above 1 ug/L during all three rain events in Round 1. The concentrations of detected phthalates in runoff from the treated wood shake panel (TWO) declined during Round 2, indicating that the phthalates detected in Round 1 had largely leached out of this roofing material.

After the first few months, phthalates did not leach from the roofing materials evaluated in this study. Phthalates measured in runoff from the new roofing materials assessed were near the ability of the method to quantify them and likely represent background conditions.

PBDEs

PBDEs are semi-volatile compounds that sorb to small particles, such as dust, and are transported with the particles and frequently found in measurements of aerial deposition.

In this study, PBDE congeners were detected rarely and only at concentrations less than the reporting limit (RL) during Round 1. No PBDE congeners were detected in runoff from any roofing panels during the three rain events sampled in Round 2.

The roofing materials evaluated in this study did not leach PBDEs to runoff. The PBDEs detected in runoff are likely a result of spatially heterogeneous aerial deposition. The impact of aged roofing materials cannot be determined from this study.

Ecology learned that PBDEs were not part of the formulation of the TPO evaluated in this study (RTF, pers. comm., 2013), but may be included in some TPO formulations as evidenced from the bromine detected in the XRF analysis (Winters and Graunke, 2014). Thus, an evaluation of TPO that has PBDE-flame retardants in its formulation should be conducted.

Conclusions

With data gathered from a total of 20 rain events during 2013-2014, Ecology established a baseline of concentrations of metals and organic compounds in runoff from new roofing materials for climatic conditions in the Puget Sound basin. While Ecology found elevated concentrations of metals in runoff from a few of the roofing materials, levels in runoff from the majority of the roofing materials tested was not elevated above levels in the glass control panels. Generally, Ecology measured elevated concentrations of copper and arsenic in runoff from the treated wood shake panel (TWO), arsenic in runoff from the PVC panel, copper in runoff from the copper panel (CPR), and zinc in runoff from the Zincalume® (ZIN) and EPDM (EPD) panels. Concentrations of organics in runoff from the roofing panels were low and generally not distinguishable from concentrations from the control panels.

Ecology found that asphalt shingle (AS^A), built-up (BUR), modified-built-up (BUA and BUS), TPO without brominated flame retardant (TPO), concrete tile (CTI), and untreated wood shingle (WOS) roofing panels did not release elevated levels of the metals or organic compounds evaluated in runoff. However, asphalt shingle roofing materials with algae-resistant (AR) copper granules do release copper. The copper-releasing granules used in this roofing material can help prevent algae from developing on a roof but are not effective in preventing moss formation.

Statistical comparisons between concentrations in runoff from the roofing materials and from the control panels inherently assume that concentrations in runoff from the control panels measure atmospheric deposition. The statistical differences identified do not address whether the runoff exceeds (does not meet) a threshold (e.g., water quality criteria, permit limits, or benchmarks). Such comparisons would require additional understanding of the fate and transport of the metals. Panel-specific statistical comparisons and conclusions concerning metals are described below.

Metals Released from Steep-Slope Panels

- The asphalt shingle panel with AR (AAR) released significantly higher concentrations of arsenic (0.04 to 2.96 ug/L) and copper (8.4 to 193 ug/L) than the steep-slope control panel over the 20 rain events. Copper concentrations in runoff from the AAR panel declined, but not significantly, in Round 2. Runoff from this panel had significantly lower zinc concentrations in Round 2.
- The replicate asphalt shingle panels without AR (AS^A) released significantly higher concentrations of copper (0.4 – 11 ug/L) than the steep-slope control panel across both sampling rounds. Overall, the three asphalt shingle replicate panels released significantly lower concentrations of copper in Round 2 than in Round 1.
- The copper panel (CPR) released copper ranging in concentration from 1,035 to 4,220 ug/L; these concentrations were significantly higher than the control panel. Copper concentrations in the runoff did not decline significantly in Round 2.
- Arsenic concentrations in runoff from the concrete tile panel (CTI) ranged from 0.04 to 3.0 ug/L, significantly higher than the control panel. Lead concentrations released from the

CTI ranged from 0.1 to 2.4 ug/L over the 20 rain events. These were also significantly higher than those released by the control panel.

- The painted galvanized metal panel (PAZ) released concentrations of zinc that ranged from 18 to 194 ug/L and were significantly higher than zinc concentrations from the control panel. Zinc concentrations in runoff from the PAZ panel increased significantly in Round 2.
- The manufacturers preserved the treated wood shake panel (TWO) with chromated copper arsenate (CCA). The treatment process met the substantive portions of the best management practices (BMPs) prescribed by the Western Wood Preservers Institute (WWPI). This panel released significantly higher concentrations of arsenic (72 to 4,690 ug/L), copper (262 to 3,190 ug/L), cadmium (0.05 to 0.31 ug/L), and zinc (2.0 to 26 ug/L) than the control panel. The concentrations of all four of these metals declined significantly in runoff collected during Round 2, indicating that some of these metals had leached out of the treated wood.
- Zinc concentrations in runoff from the wood shingle panel (WOS) ranged from 3.8 to 17 ug/L, significantly higher than the control panel during Round 1. Zinc concentrations in runoff from this WOS panel declined significantly in Round 2.

Metals Released from Low-Slope Panels

- None of the concentrations of metals in runoff from the three built-up and modified built-up roofing panels (BUR, BUA, and BUS) was significantly higher than concentrations in the low-slope control panel.
- The EPDM panel (EPD) released significantly higher concentrations of zinc (15 to 313 ug/L) than the low-slope control panel across both rounds of the study. The zinc concentrations released from this panel declined significantly in Round 2. Zinc is used as a catalyst in manufacturing EPDM and is likely released from the material over time.
- The PVC panel released concentrations of arsenic that ranged from 21 and 117 ug/L and zinc that ranged from 1.4 to 12 ug/L. Both arsenic and zinc concentrations were significantly higher than those released from the control panel across both rounds of sampling. The PVC panel released significantly lower concentrations of arsenic in Round 2, indicating that the arsenic which serves as a biocide in the PVC matrix was leaching. Zinc concentrations also declined significantly in Round 2.
- None of the concentrations of metals released from the TPO panel was significantly higher than those released from the low-slope control panel.
- The Zincalume® (ZIN) panel released concentrations of zinc ranging from 38 to 578 ug/L that were significantly higher than those from the low-slope control panel across both rounds of sampling. Zinc represents one of two metals in the Zincalume® alloy. Zinc concentrations did not decline significantly during Round 2 of the study.

Concentrations of lead in runoff from the glass control panels were significantly higher than a number of roofing panels, indicating possible leaching from the glass matrix.

Correlations between Metals and Rain Event Properties

For some metals and roofing materials, statistically significant correlations were identified. While these were not consistent across all metals or roofing materials, they correspond to literature reports. Ecology identified significant correlations between total metals concentrations and:

- Total precipitation (inverse correlation)
- Peak rain intensity (inverse correlation)
- Length of the antecedent dry period (positive correlation)

Total Metals Released to the Runoff

Ecology calculated the total metals released to runoff for those roofing materials with significantly higher metals concentrations in runoff than the control panels. Ecology recognized that release rates should not be broadly applied for the following reasons:

- The release rates changed with the aging of the panels, even in the short one-year period from the beginning of the study.
- Correlations between concentration and amount of precipitation, its intensity, and antecedent dry period likely result in varying concentrations. Using median, maximum, or minimum values to calculate whole Puget Sound basin releases may not accurately represent the conditions within the basin.
- The panels used in this study represent a run-length of less than 3 meters, much less than on many residential or commercial roofs. Longer run-length roofs would likely release greater loads of metals than those calculated in this study.

Comparison with the Puget Sound Toxics Assessment

The concentrations of metals in runoff obtained for Round 2 were compared to concentrations used to estimate releases within the Puget Sound basin from the Puget Sound Toxics Assessment (Ecology, 2011a). Only copper concentrations in runoff from the copper panel (CPR) were similar to those used to establish releases within the Puget Sound basin. With this single exception, the comparisons revealed that concentrations used in the Puget Sound Toxics Assessment (Ecology, 2011a) ranged from 30% to three orders of magnitude higher. However, runoff concentrations used to estimate releases within the Puget Sound basin (Ecology, 2011a) were based predominantly on roofing systems (full-scale roofs with components), rather than roofing materials alone.

Because concentrations in runoff depend on a number of factors – including the specific roofing material and components, age of the materials, length of the roof, angle of roof installation, and the climatic conditions described above – application of literature runoff concentrations to Puget Sound basin-wide releases should be undertaken cautiously.

Organic Compounds

Concentrations of PAHs in runoff from new roofing panels were low and generally not distinguishable from concentrations from the control panels, even in those roofs which have asphalt components (such as asphalt shingle, built-up, and modified built-up roofing). Median total PAH concentrations in runoff from all but one panel appeared to increase (but not significantly) in Round 2 over those measured in Round 1.

Concentrations of phthalates in runoff from the roofing panels were low across all panels. Phthalates observed in runoff from the treated wood shake panel (TWO) in Round 1 were no longer distinguishable from the steep-slope control panel in Round 2 of the study.

During Round 1, PBDEs in runoff from the roofing panels were low and not distinguishable from concentrations from the control panels. During Round 2, no PBDEs were detected in runoff from any of the roofing panels.

Recommendations

Many of the new roofing materials evaluated in this study released concentrations of total arsenic, cadmium copper, lead, and zinc that differed between Rounds 1 and 2, indicating a year of aging already has impacts on runoff quality. As roofing materials continue to age, concentrations of metals released may change over the 10-year to 30-year life of a roof. Ecology recommends that the impacts of aging on the release of total metals continue to be monitored. Monitoring can be continued at intervals at the Washington Stormwater Center, where the roofing panels have been relocated.

While the new roofing materials evaluated in this study do not appear to release substantial concentrations of organics, these compounds may become more leachable as the roofing materials age. The impact of aging on the release of PAHs from roofing materials should be evaluated, but at less frequent intervals. Greater specificity for future monitoring of both metals and organics is described in Winters and Graunke (2014).

Ecology learned that PBDEs were not part of the formulation of the TPO roofing evaluated in this study (RTF, pers. comm., 2013) but may be included in some TPO formulations, as evidenced from the bromine detected in the XRF analysis (Winters and Graunke, 2014). Thus, an evaluation of TPO roofing that has PBDE-flame retardants in its formulation should be conducted to determine its leachability.

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 assess 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 Task Force (RTF) provided the following additional recommendations:

- Evaluate fate and transport of those metals that, based on their concentration and/or their abundance in the region, may impact fresh and marine waters of the Puget Sound basin, as also recommended by some members of the RTF in Windward (2014).
- Assess the potential contributions of after-market roofing treatments including illegal or non-approved roofing treatments.
- Develop educational materials for appropriate use of maintenance and moss control products.
- Monitor UV intensity as part of roof aging studies.
- Assess the effectiveness of mesocosm or bioretention columns (at the WSU Stormwater Center) in removing metals in runoff from some of the roofing panels.
- Because both scale and roofing components appear to play significant roles in releases, consider a full-scale roofing system study, particularly for roofing systems on the larger commercial buildings, such as galvanized metal, Zincalume®, and EPDM. Secondly, researchers should update the relative usages of specific roofing types in the Puget Sound basin. Finally, researchers should pair these data sets to estimate releases from roofing systems within the Puget Sound basin.

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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 Total Maximum Daily Load (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.

Round 1: In this study, Round 1 refers to data collected during 10 rain events between February and April 2013.

Round 2: In this study, Round 2 refers to data collected during 10 rain events between October 2013 and January 2014.

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

AAR	Asphalt shingle roof without algae resistant copper-containing granules
APP	Atactic polypropylene roofing
AR	Algae-resistant
ARMA	Asphalt Roofing Manufacturers Association
AS^A	Asphalt shingle roofs, the average of the three replicates
BMP	Best management practice
BUA	Modified built-up roof with APP granulated cap sheet
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
DEHP	Bis (2-ethylhexyl) phthalate
DI	Distilled, deionized
DQO	Data quality objective
e.g.	For example
EAP	Environmental Assessment Program
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
EPDM	Ethylene propylene diene terpolymer; the "M" in EPDM indicates a class of rubber having a saturated chain of the polymethylene type.
et al.	And others
GLO	Glass control roof, low-slope
GST	Glass control roof, steep-slope
HDPE	High density polyethylene
HVAC	Heating, ventilation, and air conditioning
i.e.	In other words
ID	Identification
MDL	Method detection limit
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
MS	Matrix spike
MSD	Matrix spike duplicate
NADP	National Atmospheric Deposition Program
NEP	National Estuary Program
PAH	Polycyclic aromatic hydrocarbon
PAZ	Painted galvanized steel roof
PBDE	Polybrominated diphenyl ethers
PVC	Polyvinyl chloride
QA	Quality assurance
QC	Quality control
RL	Reporting limit
RPD	Relative percent difference
RSD	Relative standard deviation
RTF	Roofing Task Force
SBS	Styrene butadiene styrene
SPRI	Single Ply Roofing Institute
TPO	Thermoplastic polyolefin roofing
TWO	Treated cedar shingle roof, treated with CCA
WOS	Cedar shingle roof

WSU	Washington State University
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
L	liter
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
ug/L	micrograms per liter (parts per billion)
uS/cm	microsiemens per centimeter