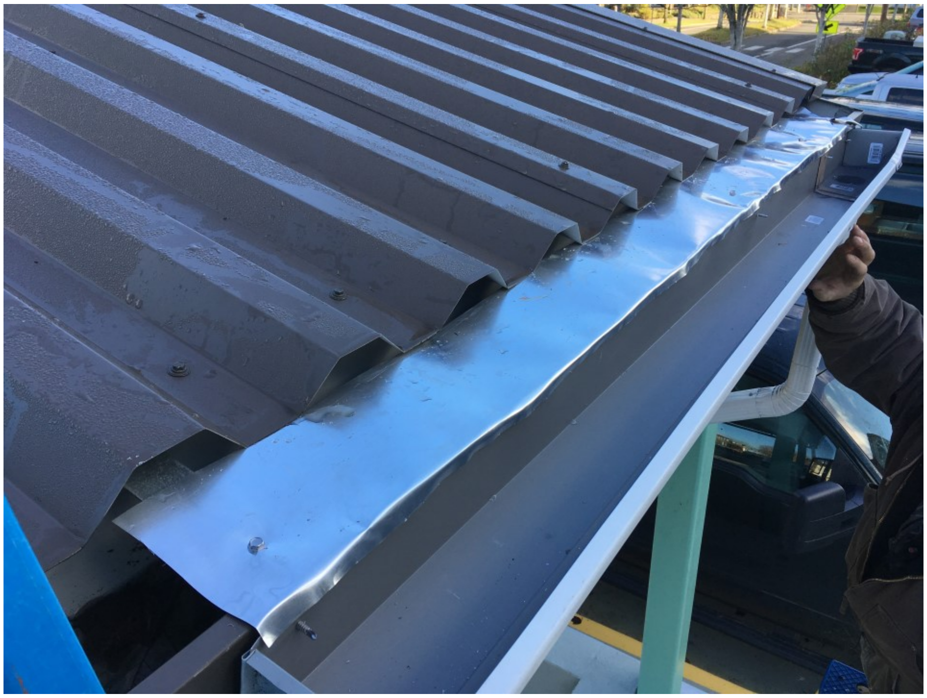
DEPARTMENT OF ECOLOGY
State of Washington

Copper and Zinc in Urban Runoff

Phase 2 — Rainwater Washoff Monitoring



June 2019
Publication 19-03-008

Publication Information

This report is available on the Department of Ecology's website at:
https://fortress.wa.gov/ecy/publications/SummaryPages/1903008.html.

Data for this project are available in Ecology's EIM Database. Study ID: ABOO0001.

The Activity Tracker Code for this study is 16-066.

This project has been funded wholly or in part by the U.S. Environmental Protection Agency (EPA) under the National Estuary Program (NEP) cooperative agreement # PC-00J899 with the Washington State Department of Ecology. The contents of this document do not necessarily reflect the views and policies of EPA, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Suggested Citation:
Bookter, A., and D. Serdar. 2019. Copper and Zinc in Urban Runoff: Phase 2 – Rainwater Washoff Monitoring. Publication 19-03-008. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/SummaryPages/1903008.html.

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Cover photo: Andy Bookter.

Copper and Zinc in Urban Runoff

Phase 2 — Rainwater Washoff Monitoring

by
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Acknowledgments

The authors of this report thank the following people for their contributions to this study:

- Greg Bailey (Bailey General Contractors)
- Chris Baird and Peter Brooks (City of Lacey)
- Dave Boyer, Mark Fromme, and Anthony Seward (Department of Enterprise Services)
- Mike Boyer (Cirque Climbing Gym)
- Joe Collins and Damon Smith (Callisons)
- Joelle Hughes and Robin Vaughn (Meconi's)
- Kimberly Gould (The Kirkbride Group, Inc.)
- Erin Larson
- Erin Fossen, Marilyn McIsaac, and Matt Polley (Fresenius Medical Care)
- Diana Kannenberg and Brandy Hildebrand (Avenue5 Residential)
- Tyler Ortiz
- Rite Aid Pharmacy
- Brian Sanda (Community Action Council)
- Caroline Sun
- Mark Biever (Thurston County)
- Brian Eko, Dean Martinolich, Monty Sabin, and Brian Westberg (North Thurston School District)

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- Steve Adams
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- Dan Dugger
- Brandee Era-Miller
- Lisa Euster
- Ruth Froese
- Steve Fry (retired)
- Kimberly Goetz
- Amy Hargrove
- Will Hobbs
- Meredith Jones
- Matthew Kogle
- Joan LeTorneau (retired)
- Sean Lundblad
- Ron McBride
- Mike McKay
- Jim Medlen
- Dean Momohara
- Dale Norton
- Jeanne Ponzetti
- Ray Powers
- Nancy Rosenbower
- Debby Sargeant
- Leon Weiks
- Andrew Wineke
- Tim Zornes

Executive Summary

Enrichment of aquatic systems with copper and zinc can have adverse effects on a variety of organisms in both freshwater and marine environments. In the Puget Sound region, copper is of particular concern due to sublethal effects on salmonids in freshwater. These effects can occur at low concentrations, often below criteria established to protect aquatic organisms (Meyer and Deforest, 2018). A recent review of data from the Puget Sound basin indicates that copper and zinc in stormwater are often found at levels exceeding water quality criteria for the protection of aquatic life, particularly in commercial and industrial areas (Hobbs et al., 2015).

To address concerns about toxic chemical contamination of aquatic systems, the Washington State Department of Ecology (Ecology) along with other agencies conducted several studies to assess releases of toxic chemicals from nonpoint sources. The *Puget Sound Toxics Loading Assessment* (PSTLA; Norton et al., 2011a) calculated estimates of copper and zinc releases from various materials and activities, as well as information on delivery and loading of copper and zinc to Puget Sound. One of the important findings suggested in the PSTLA study, based on a literature review, was that building roofs released large quantities of zinc, and copper to a lesser degree. Due to uncertainty about these findings, Ecology decided more information was needed to assess this conclusion before developing possible source control actions.

Results from the PSTLA study prompted Ecology to conduct a rigorous study of runoff from roofing materials, using a variety of experimental roof panels (Ecology Roofing Study; Winters et al., 2014). The Ecology Roofing Study found that most common roofing materials released small quantities of copper, zinc, and other chemicals. However, some data gaps remained regarding chemical releases from older roofing materials, roofs with longer runs and more contact with rainwater, and the impact that additional roofing components not analyzed (e.g., exposed fasteners, flashing) might have in real-world situations.

Based on results of PSTLA and the Ecology Roofing Study, a number of data needs were identified in order to address nonpoint sources of copper and zinc. In particular, the release of copper and zinc from specific nonpoint sources in the Puget Sound region were still unknown. Ecology began the *Copper and Zinc in Urban Runoff* study in 2016 to address these data gaps. The *Copper and Zinc in Urban Runoff* study consists of two parts: *CuZn Phase 1* and *CuZn Phase 2*. The initial phase (*CuZn Phase 1*) was a "desktop" effort focused on nonpoint sources confined to a relatively small industrial/commercial sub-basin in the southern Puget Sound region. Release rates were estimated from literature values, GIS analysis, and local precipitation data (Bookter, 2017a).

The present study, *CuZn Phase 2*, is a field sampling effort intended to fulfill some of the recommendations from the *CuZn Phase 1* report. Sampling was conducted to ground-truth some of the copper and zinc release estimates derived in *CuZn Phase 1*. To achieve this, rainwater washoff was sampled during six rain events in 2018 and analyzed for copper and zinc. The following components of the built environment were sampled:

- Building roofs
- Building siding
- Roof gutters
- Light standards
- Chain-link fencing

Findings and Conclusions

Washoff water was collected in 99% (104 of 105) of attempts to collect roof and gutter samples, 56% (40 of 72) of siding samples, and 90% (27 of 30) chain-link and light standard samples. Total copper and zinc were detected in all washoff samples, and dissolved copper and zinc were detected in all samples for which they were analyzed.

Among all materials analyzed, copper concentrations were much higher in washoff from newer (<5 years old) asphalt composite roofs containing algae-resistant granules. Zinc concentrations in washoff from uncoated galvanized materials (chain-link and light standards) were much higher than in washoff from other materials.

Copper and zinc concentrations in washoff were combined with measurements of washoff volume and surface areas to derive release rates for all materials analyzed (Table ES-1). These release rates were then used to calculate annual releases on a mass basis (i.e., loads) in the study area.

Results from *CuZn Phase 2* suggest that the overall magnitude of copper and zinc releases from the sampled materials appears to be much lower than previously estimated in the PSTLA and *CuZn Phase 1* studies. The estimated median annual release from all materials of interest within the 18.6 km^2 (7.2 square-mile) study area is approximately 6 kg copper (range 0.1–300 kg) and 70 kg zinc (range 20–500 kg). In contrast, the *CuZn Phase 1* study estimates, derived from literature, were 40 kg copper (range 4–600 kg) and 300 kg zinc (range 80–1,100 kg).

Both phases of the study conclude that the bulk of copper released from the materials analyzed would originate from asphalt shingle roofs with algae-resistant granules. For zinc, the *CuZn Phase 1* study estimated nearly equal releases stemming from roofing, siding materials, and chain-link fencing. However, results of the present study suggest the bulk of zinc release originates from uncoated chain-link fencing. The *CuZn Phase 1* study appears to overestimate releases from building materials, particularly siding.

Table ES-1. Total copper and zinc release rates for materials sampled during storm events for the *CuZn Phase 2* study.

Material category	**Material type**	**Total copper release rate (mg/m²/yr)**			**Total zinc release rate (mg/m²/yr)**		
		Min	***Median***	***Max***	***Min***	***Median***	***Max***
Roofing and Gutter	Asphalt shingle with AR <5 yrs old	4.0	120	1,100	2.3	7.4	99
	Asphalt shingle with AR >10 yrs old	0.28	5.9	87	2.3	34	270
	Painted metal <5 yrs old	0.015	1.6	3.7	0.92	30	509
	Painted metal >10 yrs old	0.058	0.72	8.3	6.6	34	1,400
	Ethylene propylene diene terpolymer	0.27	4.0	15	4.5	140	280
	Thermoplastic polyolefin	0.050	1.0	7.9	0.67	11	79
	Painted metal gutter	-2.5[a]	0.16	1.3	-32[a]	22	38
Siding	Painted fiberboard	0.0095	0.016	0.084	0.011	4.2	16
	Painted steel < 5 yrs old	0.0028	0.017	0.30	0.19	0.53	7.0
	Painted steel >10 yrs old	0.013	0.037	0.21	0.061	0.53	34
	Painted wood	0.0082	0.026	0.031	0.092	0.42	1.2
Other	Unpainted chain-link fencing	0.086	0.53	1.6	280	930	1,700
	Unpainted galvanized light standards	0.032	0.16	0.32	100	510	1,000

AR = algae-resistant granules

[a] Release rates were higher in the roof than in the roof/gutter combination.

From this sampling effort, the following conclusions can be drawn:

1) Overall, rain washoff from most roofing materials in the built environment does not contain high concentrations of copper or zinc compared with literature-based estimates (e.g., PSTLA [Norton et al., 2011a] and *CuZn Phase 1* [Bookter, 2017a]). This is consistent with findings from the Ecology Roofing Study (Winters et al., 2014).
2) Some roof types do release appreciable quantities of copper and zinc per unit area.
    a. Copper from newer asphalt shingle roofs (<5 years old) that use algae-resistant granules release copper at rates up to two orders of magnitude higher than other roof types analyzed.
    b. Copper releases from algae-resistant asphalt roofs appear to diminish as the roof ages. This is supported by the finding that copper from older asphalt shingle roofs (>10 years old) that use algae-resistant granules release copper at rates an order of magnitude lower than newer material.
    c. Zinc can be released at high concentrations by older painted metal roofs (30 years old). However, this finding is based on a single roof at this age. Five newer painted metal roofs (≤12 years old) or their companion metal painted gutters did not release high concentrations of zinc.
3) Washoff from painted siding has higher concentrations of zinc than roof washoff; copper concentrations are generally low. While not investigated for the present study, it is possible

that weathered paint is the main source of zinc from siding washoff.

4) Materials that are composed almost exclusively of galvanized steel—chain-link fencing and light standards in the case of the present study—release high quantities of zinc but little copper. However, it does not appear that there is substantial enrichment of zinc in roof washoff due to rainwater contact with ancillary roofing components, such as fasteners and flashing, that might also be composed of galvanized steel.
5) Older materials composed of exposed or painted metals generally release more zinc than newer materials.
6) Most of the copper (70% on average) and zinc (90% on average) in washoff from all materials is in the dissolved form.
7) Mass quantities of copper and zinc released annually from all materials analyzed in the study area are lower than those from literature-based estimates (e.g., PSTLA and *CuZn Phase 1* studies).
8) The PSTLA study overestimated mass zinc releases from roofing in the Puget Sound basin.
9) Results of the present study provide a better indicator of regional copper and zinc releases than those typically found in the published literature.

Recommendations

To set priorities to reduce initial release of copper or zinc from materials and activities, several questions should be considered: What materials or activities are likely to release the most copper or zinc? Are they released in a form or location where they can become mobile? Are there known impacts to surface waters due to their release from specific materials or activities?

The weight given to each question might depend on the goals of source control efforts or investigations to assess sources. For the present study, only the initial question was addressed (What materials or activities are likely to release the most copper and zinc?), and only selected source materials were investigated. As a result, contextualization is limited and the importance of the selected materials as source control priorities is thus limited as well. Future studies need not address all elements of copper and zinc releases and full assessment of their fate and transport, but more consideration to these points may yield better information for source control priorities.

Investigators may want to consider using artificial rainwater for some materials if additional washoff sampling is desired. Once there is a high degree of confidence that artificial rainwater sampling provides a suitable substitute for storm washoff, artificial washoff sampling would provide a number of benefits. Sampling could be conducted at any time and would not necessitate pre-storm setup. Adequate washoff volume could easily be generated from vertical surfaces. Sample collection devices could be smaller and simpler, and could be more easily isolated from contamination.

To assess chemical contributions from atmospheric deposition, it is recommended that sampling devices be deployed at each location where materials are sampled. This would provide a more accurate picture of site-specific atmospheric deposition and would help assess any contributions from localized sources. When sampling for metals, collection devices should be constructed of plastic, glass, or other non-metallic material.

Abstract

A two-phase study was conducted to assess the release of copper (Cu) and zinc (Zn) in the urban environment. The initial phase (Phase 1) consisted of literature research, GIS analysis, and local precipitation data. The goal of Phase 1 was to identify the major anthropogenic sources of copper and zinc and estimate the quantities released in a small urban watershed. A second phase (Phase 2) employed field sampling to ground-truth the Phase 1 estimates. This report details findings from the field sampling of copper and zinc released from a select group of materials in the built environment.

Materials selected for field sampling included four types of building roofs, three types of siding, roof gutters, uncoated galvanized chain-link fencing, and galvanized light standards. Rain washoff from these materials was collected during five storms (six for siding) during 2018. Siding washoff generated using artificial rain was also analyzed. Atmospheric deposition collectors were deployed in order to estimate the contribution from this source. Nearly all of the sampling sites were located within the same 18.6 km^2 watershed in Thurston County, Washington.

Rainwater washoff from most materials contained low concentrations of both copper and zinc. Exceptions were high concentrations washed from newer asphalt roofs with algae-resistant granules and high zinc concentrations in washoff from galvanized structures (chain-link fences and light standards). Results indicate that within the study watershed small quantities of copper and zinc are released annually from the materials examined. The rates of copper and zinc release for all of the materials sampled are lower than those estimated in Phase 1. Recommendations are included for using copper and zinc release data in prioritizing source control actions.

Introduction

Identification of Problem

Human activities have increased the levels of copper (Cu) and zinc (Zn) in the aquatic environment through both point (e.g., end-of-pipe discharges, dumping) and nonpoint (diffuse) releases. Historical reconstruction through sediment coring indicates that substantial aquatic enrichment of both copper and zinc began in the late nineteenth century, coinciding with industrial development in the Puget Sound area (Lefkovitz et al., 1997). Loading of copper and zinc into Puget Sound reached a peak in the mid-twenthieth century, then began to decline following promulgation and implementation of environmental regulations designed to reduce point source pollution.

The trend toward recovery to natural copper and zinc levels in aquatic systems, however, may be slowing (Brandenberger et al., 2008). Likely reasons include the rapid urbanization of the Puget Sound basin and the relative ineffectiveness of regulations to control nonpoint pollution that accompanies increased development. For instance, a recent review of stormwater data in the Puget Sound basin indicates that copper and zinc are often found at levels exceeding water quality criteria for the protection of aquatic life, particularly in commercial and industrial areas (Hobbs et al., 2015).

Enrichment of aquatic systems with copper is a particular concern in the Puget Sound region due to its adverse effects on a variety of organisms in both freshwater and marine environments. A growing body of evidence indicates that low levels of copper in freshwater can exert sublethal effects in salmonids. These effects include avoidance of copper-containing waters and olfactory impairment, which can lead to reductions in predator-avoidance or food-finding behaviors (Sandahl et al., 2007; Tierney et al., 2010). Effects in freshwater can occur at concentrations near typical ambient levels of dissolved copper and often below criteria established to protect aquatic organisms (Meyer and Deforest, 2018).

Zinc does not appear to be as toxic as copper at typical concentrations found in the Puget Sound region, but areas of potential hazard exist where concentrations are elevated (Norton et al., 2011a, 2011b). There is little or no evidence that zinc in freshwater impacts olfaction in salmonids or causes other adverse sublethal effects, such as those resulting from copper exposure (e.g., Lorz and McPherson, 1977). However, avoidance behaviors may be elicited in salmonids, such as rainbow trout (*Oncorhynchus mykiss*) exposed to low levels of zinc (Sprague, 1968).

Prior Studies and Impetus for Present Work

In order to address nonpoint sources of copper, zinc, and other chemicals in the Puget Sound basin, the Washington State Department of Ecology (Ecology) and other agencies conducted the *Puget Sound Toxics Loading Assessment* (PSTLA) from 2007 to 2011 (Norton et al., 2011a). PSTLA was a broad-scope study designed to assess the sources of toxic pollutants, the important delivery pathways for each chemical, and a systematic evaluation of potential hazards to aquatic organisms. Copper was identified as a top priority for near-term action due to 1) its potential to harm aquatic organisms at observed concentrations; 2) the large quantities delivered to Puget Sound, primarily through surface runoff, with the highest concentrations measured in runoff from commercial and industrial areas; 3) the large quantities released to the environment, particularly from vehicle brake pads, nonagricultural pesticide use, leaching from roofing materials, leaching from plumbing, and from anti-fouling paint in marine vessels; and 4) the relative abundance of opportunities to control these nonpoint sources of copper.

Since the initiation of PSTLA, a number of actions have been taken to reduce copper from nonpoint sources. These include the 2010 Better Brakes Law (Chapter 70.285 RCW), which requires a near-complete phase-out of copper in brake friction materials by the year 2025, and a law requiring the near-complete phase-out of copper in vessel bottom paint by 2021 (Chapter 70.300 RCW and subsequent revisions [SHB 2364]). Existing federal law already addresses copper in plumbing (Lead and Copper Rule; 40 CFR Part 141), and therefore, emphasis was not placed on additional controls for this source of copper. Pesticides containing copper were further investigated by Washington State Department of Agriculture and found to be rarely used in the Puget Sound region (McClain, 2014), rendering this an inconsequential source of copper.

The PSTLA study did not identify zinc as a high-priority chemical, due to its moderate ranking as a chemical with potential to elicit biological effects. However, zinc releases and loading were estimated to be extremely high in quantity, second only to petroleum among the chemicals addressed.

Like copper, the highest zinc concentrations were measured in runoff from commercial and industrial areas, and overall surface runoff was the primary delivery pathway for zinc to Puget Sound. The largest estimated quantities released were from leaching of roofing materials and from vehicles (mainly tire wear). The PSTLA report also noted that quantities of zinc releases might have been underestimated, because sources such as exposed galvanized materials (e.g., light standards, culverts, and guardrails) were not evaluated.

Authors of the PSTLA report recommended that monitoring be conducted to assess chemicals released from roofing materials. In response, Ecology conducted a study during 2013 and 2014 to evaluate chemicals leached from individual roofing materials (hereafter referred to as the Ecology Roofing Study [Winters et al., 2014]). This was accomplished by sampling rainwater washed off of a variety of experimental roofing panels; other roofing system components (e.g., flashings, gutters, downspouts, fasteners, HVAC systems) were not included in these experimental roof constructions.

With a single exception (copper roofing), release rates of copper, zinc, and other chemicals were much lower — often by orders of magnitude — than those used to calculate basin-wide releases in the PSTLA study. The authors of the Ecology Roofing Study suggested that the lack of a full complement of roofing components analyzed, short roof runs (i.e., length of roof), and lack of representative roof ages were among the possible explanations for the differences. Recommendations to address these variables were among those proffered for further evaluation.

CuZn Phase 1 Study

Based on results of PSTLA and the Ecology Roofing Study, a number of data needs were identified to address nonpoint sources of copper and zinc. In particular, the relative importance of copper and zinc releases from specific nonpoint sources in the Puget Sound region was still unknown. Ecology launched the *Copper and Zinc in Urban Runoff* study in 2016 to address these data gaps. The *Copper and Zinc in Urban Runoff* study consists of two phases. The initial phase (*CuZn Phase 1*) was a “desktop” effort focused on nonpoint sources confined to a relatively small industrial/commercial sub-basin in the southern Puget Sound region. Release rates were estimated from literature values, GIS analysis, and local precipitation data (Bookter, 2017a).

CuZn Phase 1 estimated that 360 kg (800 pounds) of copper and 2,700 kg (5,900 pounds) of zinc are released annually from nonpoint sources in the 18.6 km^2 (7.2 square-mile) *CuZn* study area. The primary sources of copper were identified as vehicle brake wear, roofing materials, parking lots, treated lumber, building siding, and vehicle exhaust. The main sources of zinc are moss control products, building siding, parking lots, vehicle tire wear, chain-link fence, roofing materials, and vehicle brake wear. Total annual releases for each of these sources, as well as those for lesser sources, were calculated for the entire study area.

Bookter (2017a) also used a systematic approach to categorize the uncertainty and variability of each estimate reported in *CuZn Phase 1*. Sources in the built environment with the highest potential to release copper or zinc and the greatest uncertainty around the estimated loading values were recommended for further investigation. Suggested sources for monitoring in the built environment included parking lots, building roofing and siding materials, streetlights (light standards), and roof gutters.

Present Study

The present study, Phase 2 of the *Copper and Zinc in Urban Runoff* study (*CuZn Phase 2*), is a field sampling effort intended to fulfill some of the recommendations from the *CuZn Phase 1* report. Sampling was conducted primarily in the same sub-basin analyzed in *CuZn Phase 1*. Details of the sampling design, locations, and methods are discussed further in following sections and in the Quality Assurance Project Plan (QAPP; Bookter, 2017b).

Briefly, rainwater washoff from the following components of the built environment were sampled and analyzed for copper and zinc:

- Building roofs
- Building siding
- Roof gutters
- Light standards
- Chain-link fencing

The overall goal of the *CuZn* study is to identify nonpoint sources of copper and zinc in the urban environment and attempt to fill gaps in the current knowledge regarding those sources. *CuZn Phase 1* identified sources and data gaps using literature review. *CuZn Phase 2* fills some of those gaps with field data.

The focus of this study is on *primary* releases of copper and zinc. Field data on fate and transport of newly released copper or zinc is not assessed. The results from this study will inform future source control efforts in the identification and reduction of important sources of copper and zinc in urban areas. Source control prioritization should also incorporate the fate and transport of pollutants.

Project goals

The goal of *CuZn Phase 2* was to measure the quantity of copper and zinc released from various materials and structures in the urban built environment.

Project objectives

To accomplish the project goals, the following objectives were achieved:

- Measure the quantity of copper and zinc leached from specific materials in the urban environment.
- Develop release rates for copper and zinc from various materials.
- Recalculate study area loading values using new release rates.
- Compare release rates to *CuZn Phase 1* data.

Methods

Sample Design and Scope

Parameters of Interest and Sources of Chemical Release

CuZn Phase 2 was designed to assess building materials of various ages in situ and exposed to typical environmental conditions in the study area. Details of the rationale for the project sample design are in the QAPP (Bookter, 2017b). Parameters of interest were limited to copper and zinc due to their potential for adverse biological effects (particularly copper) and the magnitude of quantities potentially released from building materials. Ancillary water quality parameters analyzed included total suspended solids (TSS), dissolved organic carbon (DOC), hardness, pH, turbidity, temperature, and conductivity.

Specific sources assessed for copper and zinc release were roofs, building siding, gutters, light standards, and chain-link fencing. These sources were selected based on results of *CuZn Phase 1* (Bookter, 2017a) and data gaps identified in previous studies (Norton et al., 2011a; Winters et al., 2014). Bulk atmospheric deposition sampling was also conducted with the intention to correct for air deposition as a source of copper and zinc. Metals present in the atmosphere may be the result of nonindustrial combustion emissions, industrial emissions, or vehicle wear particles such as tire and brake dust (Ochoa Gonzales et al., 2016).

Study Area

The *Copper and Zinc in Urban Runoff* study area is an 18.6 km^2 (7.2 square-mile) portion of the lower Woodland Creek watershed in the City of Lacey and adjacent unincorporated Thurston County (Figure 1). Woodland Creek drains to Henderson Inlet in southern Puget Sound.

The study area was selected for the concentrated commercial and industrial land uses, which have been shown to have higher copper and zinc concentrations in stormwater and streams than other land uses (Herrera Environmental Consultants, Inc., 2011; Hobbs et al., 2015). In 2016, land use in the study area was 35.5% commercial/industrial, 13.6% residential, 33.9% undeveloped, 12.4% roadways, 2.9% parks, and 1.8% agricultural (Figure 2). Of the area currently developed, 66% is commercial/industrial land use. This land use profile is similar to other urban areas of the Puget Sound basin.

Bookter (2017a) used U.S. census data to estimate the 2010 population of the study area at approximately 7,600. The study area is undergoing rapid development (Collyard and Anderson, 2017).

The *CuZn* study area is located approximately halfway between Seattle, Washington, and Portland, Oregon, along the Interstate 5 corridor. The proximity to two large urban centers has made Lacey a transportation hub for major distribution companies (e.g., Target, Home Depot, Trader Joes, Harbor Wholesale Foods). In addition, Joint Base Lewis–McChord is located approximately 24 km (15 miles) north of the study area. This has resulted in increased development of large warehouses, apartment complexes, tract housing, and commercial services (e.g., big-box stores, strip malls, restaurants, banks).

The climate of the study area is temperate. Monthly average high and low temperatures range from 78°F/51°F (26°C/11°C) in August to 44°F/33°F (7°C/0.6°C) in December (Weather.com[1]). The average annual precipitation between 2003 and 2016 was 1003 mm (39.5 inches). The annual number of days of rain varied from 104 to 169 in that same period (Nat Kale, pers. comm., Thurston County Stormwater, 2018).

The study area boundary was initially drawn along hydrological boundaries for two small watersheds draining into Woodland Creek. Because the focus of the study is on sources in the built environment, the study area boundary was expanded to follow tax parcel and neighborhood borders.

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[1] https://weather.com/weather/monthly/l/Lacey+WA+USWA0217:1:US

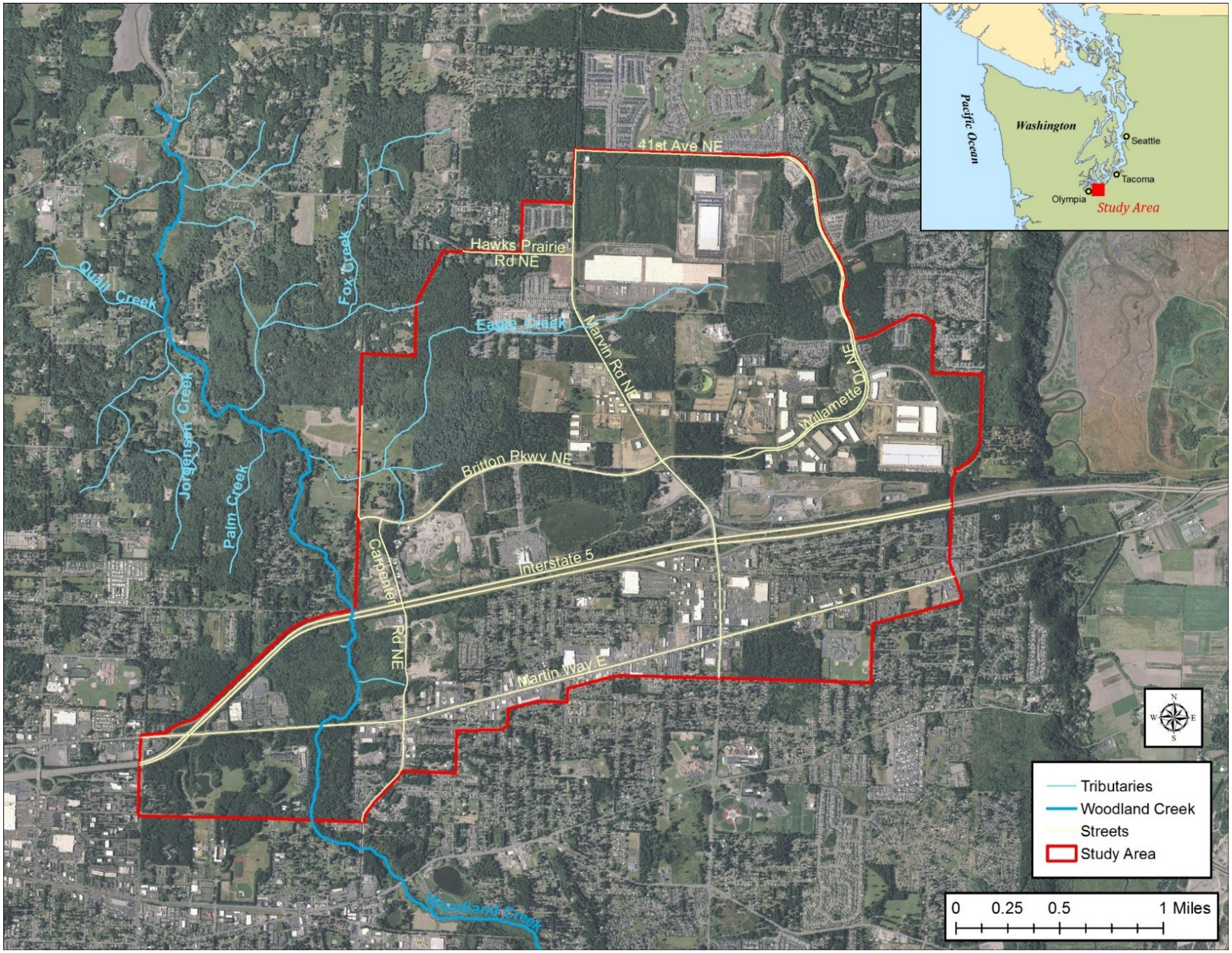

Figure 1. Map of the urban copper and zinc study area, Lacey, Washington.

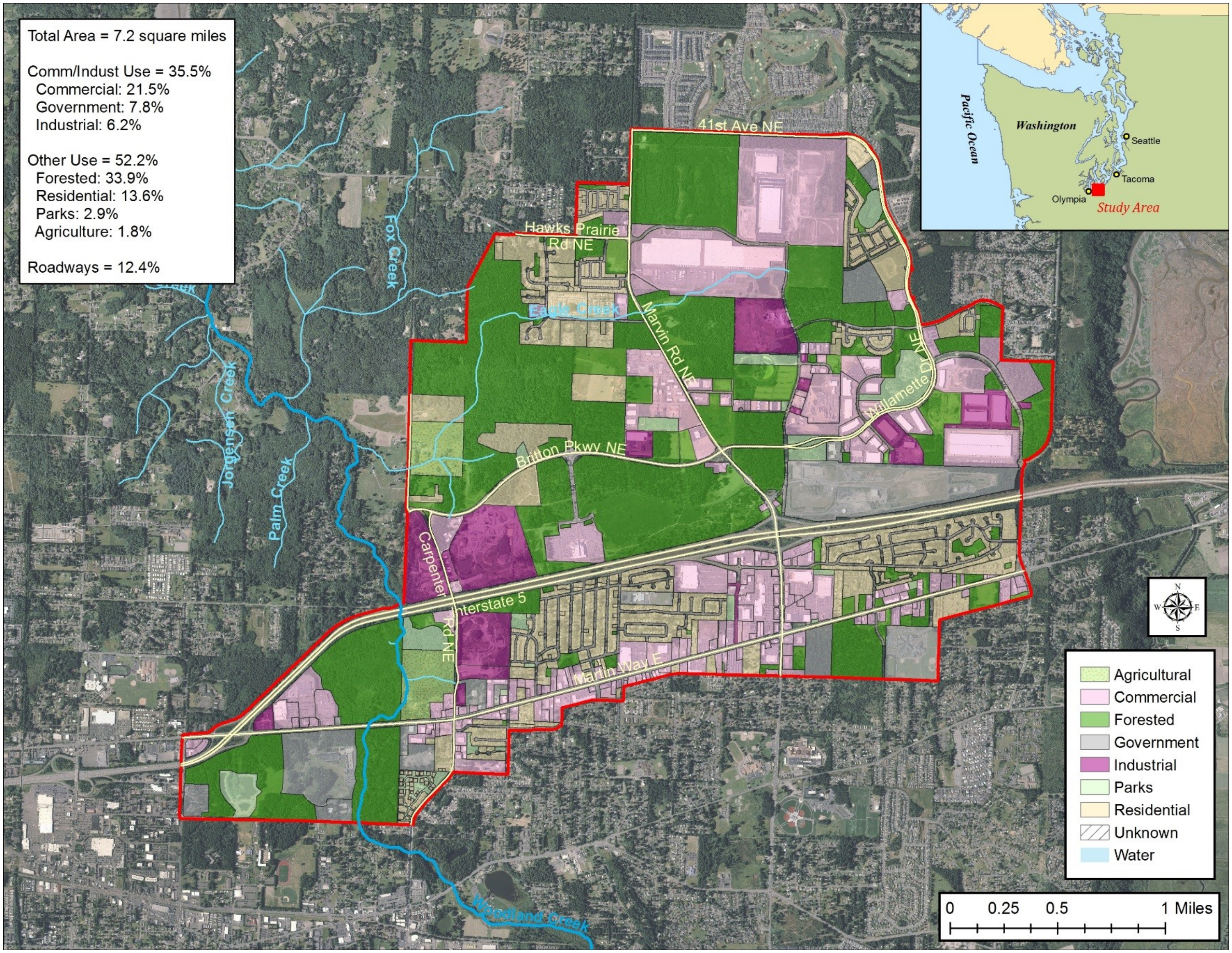

Figure 2. Map of 2016 land use in the urban copper and zinc study area, Lacey, Washington.

Material and Site Selection

Bulk rainwater washoff was collected from four different types of roofing materials, three types of siding, roof gutters, chain-link fencing, and galvanized light standards (Table 1). For two of the roof types and one siding type, both new (<5 years) and aged (>10 years) materials were sampled. Three sites were sampled for each of the materials of interest.

Table 1. Materials sampled for the *CuZn Phase 2* study.

Source	Material type	Age (years)	Number of sites	Sample events	Total samples*
Roofing	Asphalt (AAR)	<5	3	5	15
"	Asphalt (AAR)	>10	3	5	15
"	Metal	<5	3	5	15
"	Metal	>10	3	5	15
"	Polymer (EPDM)	–	3	5	14
"	Polymer (TPO)	–	3	5	15
Gutters	Metal	–	3	5	15
Siding	Painted fiberboard	<5	3	6	10
"	Metal	<5	3	6	14
"	Metal	>10	3	6	13
"	Painted wood	>10	3	6	3
Chain-link fence	Galvanized	–	3	5	13
Light standard	Galvanized	–	3	5	14
Atmospheric deposition	Bulk	–	2	6	12
Total	**–**	**–**	**41**	**5–6**	**183**

** Not including quality assurance (QA) samples.*
AAR = asphalt shingle with algae-resistant granules; Metal = painted steel; EPDM = ethylene propylene diene terpolymer; TPO = thermoplastic polyolefin

Material type, brand, and age were collected from building construction and maintenance records. Material condition was obtained from Thurston County Assessor data and through onsite observation. Sampling locations were selected based on the type of construction material, material age, the logistical convenience for sample collection, and the ability to isolate the material of interest from other sources of copper and zinc. Appendix A lists details for each location.

Roof-only monitoring sites with aluminum gutters and downspouts were given preference in order to isolate copper and zinc from interfering sources. These were moderate- to steep-sloped roofs constructed of asphalt shingles with algae-resistant granules (AAR) or painted steel (Metal).

Most commercial roofs in the study area are low-sloped and generally drained via polyvinyl chloride (PVC) or galvanized steel downspouts, which are potential sources of copper and zinc. Low-sloped commercial roofs sampled were constructed of ethylene propylene diene terpolymer (EPDM) or thermoplastic polyolefin (TPO).

Chain-link fencing selected for sampling all appeared to be of the galvanized-before-weave type, based on visual inspection.

Light standards were industrial-grade galvanized steel of the type used on major roadways. Two were located on interstate on-ramps and one was located at a large park-and-ride lot.

Bulk Washoff Collection

Passive collection systems were used to collect and store the bulk washoff during each storm event. Runoff from each monitoring site was sampled during five or six storm events from February through June 2018 (Figure 3).

Precipitation data were obtained from the Thurston County Waste and Recovery Center (WARC) located in Lacey (Nat Kale, pers. comm., Thurston County Stormwater, 2018). For days when precipitation data were not recorded at the WARC, measurements from the Olympia Airport (NOAA[2]) and a nearby Weather Underground station (Weather Underground[3]) were averaged. Storms qualifying for a sampling event had a minimum rainfall depth of 5 mm (0.2 inches) with an antecedent dry period (less than 0.5 mm of rainfall) of six hours, a modification of sampling criteria established for the Phase I Municipal Stormwater Permit (Lowe, 2010). All storms except Storm 4 (3.7 mm precipitation) met these criteria. The passive collectors were deployed preceding the onset of storms forecast to meet these sampling criteria.

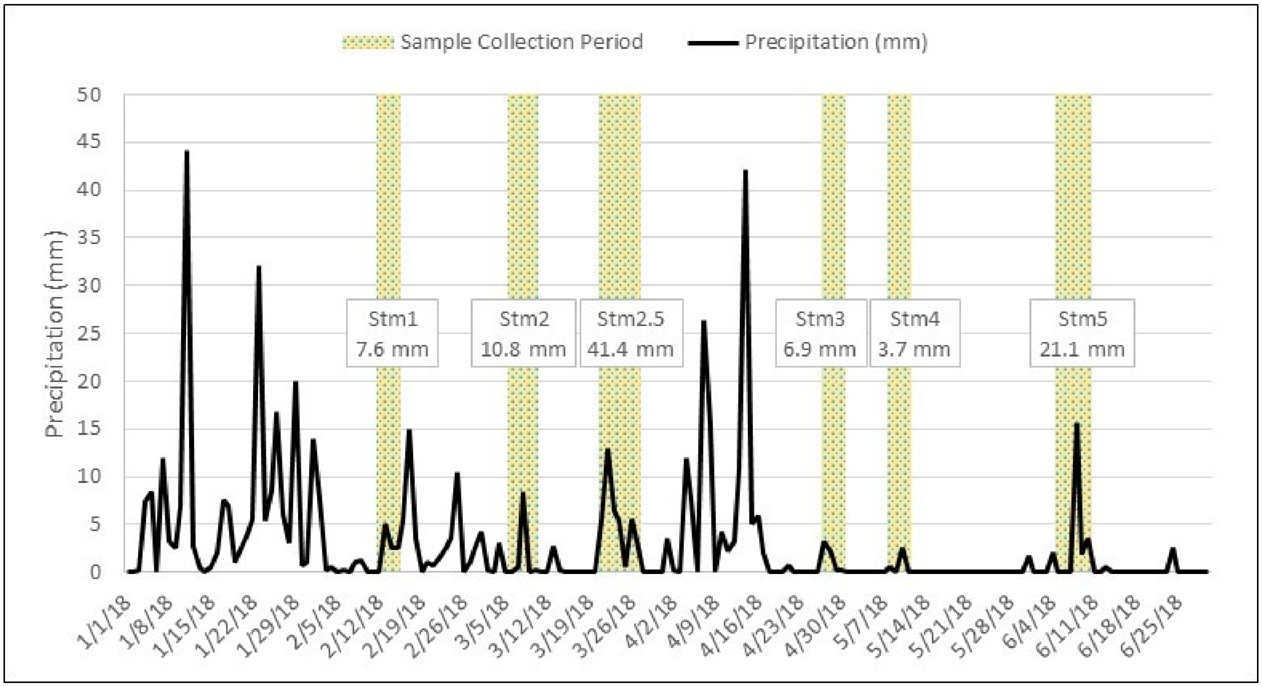

Figure 3. Precipitation (mm) in Lacey, Washington, during the 2018 *CuZn Phase 2* study. Amounts during the six bulk washoff collection storms are shown in boxes.

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[2] https://w2.weather.gov/climate/index.php?wfo=sew

[3] https://www.wunderground.com/dashboard/pws/KWALACEY34

Rainwater washoff from low-sloped commercial polymer roofs was sampled either by plugging one roof drain using a plug made of stainless steel and rubber or by constructing a washoff dam using aluminum flashing (Figure 4). Sample aliquots were then collected by compositing grab samples from the ponded stormwater. Roof sections were selected to minimize the contribution of copper or zinc from other roof components.

Figure 4. Rainwater washoff collected on a polymer roof using a dam constructed of aluminum flashing.

For moderate- to steep-sloped roofs with aluminum gutters, aluminum diverters were installed in gutter downspouts to route rainwater runoff into 55-gallon sample collection drums with modified polytetrafluoroethylene (MPTFE) liners (Welch Fluorocarbon, Inc., Dover, New Hampshire). The collection drums were lidded, with a single small opening for the downspout diverter, and shrouded with plastic wrap to ensure that only rainwater from the roofing material was collected (Figure 5).

Figure 5. Rain barrel used to collect roof washoff via a downspout diverter.

To estimate copper and zinc contributions from painted steel gutters, diversions were constructed that allowed roof washoff to be collected without contacting gutters (Figure 6). Contributions of copper and zinc from painted steel gutters were calculated as the difference between the total roof runoff (i.e., roofing and gutters) and the rainwater washoff from the roofing material alone. These calculations were made following the conversion of copper and zinc concentrations into unit area release rates. The roof and roof/gutter samples were collected from different locations on the same roof system.

Figure 6. System used to divert roof washoff without contacting the building gutter and downspout. Aluminum flashing (not visible in this photograph) was used to prevent contact with the building gutter.

Building siding locations were selected to maximize rainwater volume and reduce the copper and zinc contributions from other construction materials. The sides of buildings facing the prevailing wind direction — generally the southwest — was sampled where possible. Siding material locations were selected to avoid contact with roof washoff.

Rainwater washoff from building siding was collected by placing an aluminum pan beneath the siding drip line (Figure 7). Pans were lidded, with only the area underneath the dripline open for washoff collection.


Figure 7. Aluminum pans used to collect siding washoff.

Washoff from galvanized light standards was collected by installing aluminum foil collars near the base of the poles (Figure 8). The collar routed washoff into stainless steel funnels that drained into lidded five-gallon buckets with MPTFE liners. Buckets were lidded with a single small opening for the funnel to ensure that only washoff from the light standard was collected.

Figure 8. Aluminum foil collar used to collect washoff from galvanized light standard.

Washoff from galvanized chain-link fences was collected in aluminum pans placed below a section of fence dripline (Figure 9). Pans were lidded on either side of the fence to ensure that only washoff interacting with chain-link material was collected.

Figure 9. Aluminum pan used to collect washoff from chain-link fence.

Bulk atmospheric deposition samples were collected at two sites in the study area for each storm event. Atmospheric deposition stations were located in the southwest and northeast quadrants of the study area and elevated on building roofs to reduce the possibility of sample contamination.

Atmospheric deposition collection systems were deployed during each monitored storm event and the preceding antecedent dry period. This allowed for collection of both wet and dry deposition coupled with each sampled storm event. The collection systems were removed from the rooftops during minor precipitation events to eliminate collection of wet deposition during those storms.

Bulk atmospheric deposition samples were collected using a 45.7-cm (18-inch) diameter circular stainless steel funnel exposed to the atmosphere (Figure 10). The decontaminated funnel drained into a five-gallon bucket with a MPTFE liner. This collection system is adapted from a similar system used to sample polychlorinated biphenyls (PCBs) in the Spokane River basin (Era-Miller and Wong, 2016).

Figure 10. Bulk atmospheric deposition collector.

Sample Aliquot Collection

Sample aliquots for field measurement and laboratory analysis were collected within 24 hours of the conclusion of each sampled storm event. Bulk samples were first homogenized by agitation of the sample inside of the Teflon liner or by stirring with an acid-washed stainless steel mixing paddle for larger volumes. Aliquots of bulk samples with small volumes were poured directly from the Teflon liners or aluminum pans into individual analyte bottles. For larger volumes where direct pouring was not feasible, samples were poured into analyte bottles using decontaminated stainless steel ladles. Sample containers, sample preservation, and holding times are listed in Appendix B.

Equipment decontamination was done by scrubbing with Liquinox detergent (Alconox, Inc., White Plains, New York) followed by sequential rinses with tap water, 10% trace metals grade nitric acid (Fisher Scientific, Ottawa, Ontario), and deionized water, then wrapped in aluminum foil (dull side in) for transport into the field. Filtering for dissolved metals and dissolved organic carbon was conducted on-site within 15 minutes of sample processing using precleaned 0.45 µm filters.

Rainwater washoff samples were placed on ice immediately following aliquot collection and kept in a locked walk-in refrigerator at Ecology's Operations Center upon return from field. Samples were transported to Manchester Environmental Laboratory (MEL) with 48 hours of collection. MEL conducted analysis for total and dissolved metals (Cu, Zn), dissolved organic carbon (DOC), total suspended solids (TSS), and hardness.

Following aliquot collection for laboratory analysis, the remainder of the bulk sample was analyzed in the field for temperature, pH, conductivity, and turbidity using a YSI EXO1 multi-parameter sonde (YSI, Inc., Yellow Springs, Ohio).

Equipment and field blanks were prepared by rinsing the equipment or filtering with laboratory-provided deionized water and collecting the resultant rinsate or filtrate prior to sample collection. Rinsate from MPTFE liners, aluminum pans, and atmospheric deposition funnels was analyzed for total and dissolved metals (Cu, Zn). The filter apparatus blanks were analyzed for dissolved metals (Cu, Zn).

The field-deployed water quality sensors (pH, conductivity, and turbidity) were calibrated according to the manufacturer's recommendations before each sample collection event and checked against calibration standards at the end of each event. The pH sensor was calibrated for every sample event using a three-point calibration with standards for pH 4, 7, and 10. A single-point calibration using a 1,000 µS/cm standard was performed on the conductivity sensor. The turbidity sensor was calibrated using 0 NTU (deionized water), 126 NTU, and 1010 NTU standards. All standard solutions used were manufacturer-recommended standards.

Artificial Rainwater Washoff Sampling

Artificial rainwater washoff sampling was conducted on August 15, 2018, to supplement data on copper and zinc in siding washoff. Samples were collected from washoff generated by applying a known volume of synthetic rainwater to an isolated area of siding material.

A pressurized garden spray bottle was used to deliver one liter of artificial rainwater to each of the siding materials shown in Table 2. Washoff sampling was limited to the bottom 1 meter of siding material at each site in order to mimic the portion of siding most likely to be exposed to rain. Portions of siding to be sampled were isolated using a 1 × 0.5 m foil-sided template, yielding 0.5 m^2 of surface area washed at each site (Figure 11).

Table 2. Characteristics of siding selected for artificial rainwater washoff sampling.

Location ID*	Siding Type	Material Age (yrs)	Paint Age (yrs)	Surface area (m^2)	Volume (L)
ECHQ-SMT	Metal (painted steel)	12	12	0.5	1.0
EAGL-SFBR	Painted fiberboard (fiber cement)	4	4	"	"
CAMP-SFBR	Painted fiberboard (fiber cement)	5	5	"	"
ADON-SFBR	Painted fiberboard (fiber cement)	1	1	"	"
CIRQ-SMT	Metal (painted steel)	1	1	"	"
MILL-SWD	Painted Wood	ca. 60	15	"	"
NTA-SMT	Metal (painted steel)	2	2	"	"
NEIL-SWD	Painted Wood	50	14	"	"
CAC-SWD	Painted Wood	12	5	"	"

** See Appendix A for sampling location information.*

Figure 11. Template used to isolate siding for artificial rainwater washoff sampling.

The spray bottle was pressurized to approximately the same level at each site by replicating the amount of artificial rainwater in the sprayer at each site and pumping the same number of times. Spray width (3 cm) and distance from siding (10 cm) were consistent for each application. The angle of spray was approximately 20 degrees outward from vertical to approximate the angle of wind-driven rain.

Siding was washed twice in succession at each site in order to assess whether the initial spray washed off airborne dust and film. Samples were collected after each wash, for a total of two samples per site. Catchment of the washoff was conducted in the same manner as for the rainwater washoff sampling, using identical aluminum pans deployed without lids.

Artificial rainwater was prepared from an adaptation of that described in Davis et al (2001). The solution, with a final pH of 5.2, contained 10 µM NaCl, 5.5 µM HNO_3, and 5.5 µM H_2SO_4 in Milli-Q Reference (reverse osmosis) water. Sodium chloride and acids were trace metals grade (Fisher Scientific, Ottawa, Ontario). Sodium and chloride composition, as well as pH, were similar to those of natural rainwater in western Washington (NADP, 2017).

All washoff samples using artificial rainwater were analyzed for total and dissolved copper and zinc only. Equipment blanks were collected from the sprayer prior to sampling and at sampling completion and analyzed for total copper and zinc.

Measurement Procedures

Total and dissolved copper and zinc were prepared and analyzed by inductively coupled plasma–mass spectrometry (ICP-MS) following the protocols outlined in EPA Method 200.8 (Table 3). Dissolved organic carbon (DOC) was analyzed using a high temperature combustion/infrared analyzer, described in Standard Methods (SM) 5310B. Total suspended solids (TSS) measurements were made by drying nonfilterable residue at 103–105°C (SM 2540D). Hardness was measured by ICP–atomic emission spectrometry (EPA 200.7) and calculated using the procedure in SM 2340B.

Table 3. Methods used for laboratory and field measurements.

Location	Analyte	Typical reporting limit	Sample prep method	Analytical (instrument) method
Laboratory	Total and dissolved copper	0.1 µg/L	EPA 200.2[a]	EPA 200.8
Laboratory	Total and dissolved zinc	1–5 µg/L	EPA 200.2[a]	EPA 200.8
Laboratory	Dissolved organic carbon	0.5 mg/L	na	SM 5310B
Laboratory	Total suspended solids	1–2 mg/L	na	SM 2540D
Laboratory	Hardness (as $CaCO_3$)	0.3 mg/L	na	EPA 200.7/SM 2340B
Field*	pH	0.01 S.U.	na	pH sensor
Field*	Conductivity	0.01 µS/cm	na	conductivity sensor
Field*	Turbidity	0.1 NTU	na	turbidity sensor

EPA = U.S. Environmental Protection Agency; SM = Standard Methods for the Examination of Water and Wastewater (Baird et al., 2017).
na = not applicable; [a] For total metals only; * Reporting limits based on YSI EXO1 sensor.

Data Reduction and Reporting

Naming Conventions for Material Types

Naming conventions for building material types are based on the building component and specific material type. For example, the name assigned to metal siding is *S* (for siding) + *MT* (for metal) = *SMT*. For building materials where locations were selected for age differences, an extension was added to the material name (e.g., the name assigned to metal siding >10 years old is *SMT>10*. Naming convention for building materials and other materials are shown in Table 4.

In cases where results from a specific locations are discussed, the location identification is named using the location abbreviation plus the material type. For instance, the Natural Resources Building (*NRB*) metal roofing (*RMT*) is assigned the name *NRB-RMT*. All locations, material types, and associated names are included in Appendix A.

Table 4. Naming conventions for material types.

Building component	Material type	Assigned name	Material age (yrs)	Extended assigned name
Roofing	Asphalt shingle with algae-resistant granules	RAAR	<5	RAAR<5
"	"	RAAR	>10	RAAR>10
"	Metal (painted steel)	RMT	<5	RMT<5
"	"	RMT	>10	RMT>10
"	Ethylene propylene diene terpolymer	REPDM	--	REPDM
"	Thermoplastic polyolefin	RTPO	--	RTPO
Gutters	Metal (painted steel)	GUTT	--	GUTT
Siding	Fiberboard (painted fiber cement)	SFBR	--	SFBR
"	Metal (painted steel)	SMT	<5	SMT<5
"	"	SMT	>10	SMT>10
"	Wood (painted)	SWD	--	SWD
Chain-link fence	Galvanized steel	CNLNK	--	CNLNK
Light standard	Galvanized steel	LGT	--	LGT
Atmospheric deposition	Atmospheric deposition	ATM	--	ATM

Presentation of Results for Washoff Samples

Unless stated otherwise, all concentrations of copper and zinc in water are expressed as micrograms per liter (µg/L). All conventional parameters are expressed as milligrams per liter (mg/L).

Box-and-whisker plots are used to summarize concentrations of metals and other parameters in water, as well in other types of data analysis. Box-and-whisker plots are a useful graphical display of a data set where means, interquartile values (medians, 25th and 75th percentiles), 10th and 90th percentiles, and outliers can be compared among groups. Figure 12 shows an example box-and-whisker plot and its components.

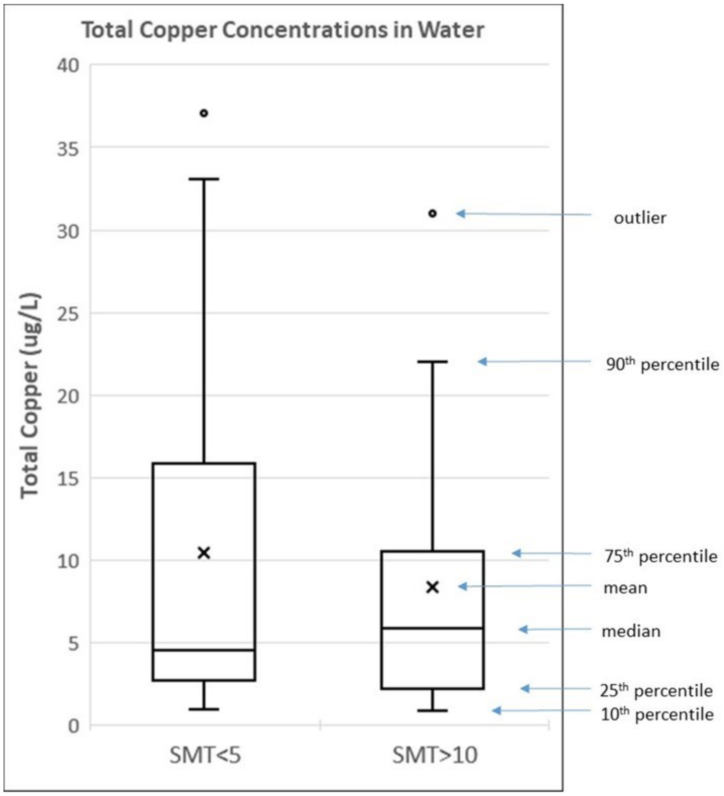

Figure 12. Example of box-and-whisker plot used to display data throughout report.

Calculation of Metals Release Rates from Different Materials

Copper and zinc unit area release rates and fluxes for atmospheric deposition were calculated as mass quantities (expressed as µg, mg, g, or kg) released from a unit surface area of each material sampled (expressed as m^2) per year.

Methods for calculating unit area release rates begin with measuring or calculating the volume of washoff for each storm event and on-site measurements of the surface area being sampled. The volume of washoff collected was measured from water accumulated in the rain barrels, buckets, or pans used to collect washoff. For locations where rooftop dams were used to collect washoff in pools, simple geometry was used to estimate the pool volumes based on the surface dimensions and depths of the pools. In some instances, rain barrels overflowed, and the volume of washoff was estimated using the amount of rainfall during the storm event and the known surface area of material being sampled (Equation 1).

(Equation 1)

$$\text{Estimated volume of storm washoff (L)} = \text{storm event precip. (mm)} \times \text{area of material sampled (m)}$$

Storm event mass release of metals is then calculated from the concentration of metals in washoff water and the washoff volume (Equation 2).

(Equation 2)

$$\text{Event mass release } (\mu\text{g}) = \text{volume of storm washoff collected (L)} \times \text{metals conc. in washoff } (\mu\text{g/L})$$

This can also be expressed as unit area release at each location (Equation 3).

(Equation 3)

$$\text{Event unit area release } (\text{mg/m}^2) = \frac{\text{event mass release of metals } (\mu\text{g})}{\text{known washoff area } (\text{m}^2)} \times \frac{\text{mg}}{1{,}000\ \mu\text{g}}$$

Once the storm event release of metals was calculated for each location and material being sampled, an annual release rate was estimated by assuming that the storm precipitation amount represented a fraction of the annual average precipitation (Equation 4).

(Equation 4)

$$\text{Annual release rate } (\text{mg/m}^2/\text{yr}) = \text{event unit area release } (\text{mg/m}^2) \times \frac{\text{annual precip. (mm/yr)}}{\text{storm event precip. (mm)}}$$

Annual mass releases (loads) for a given material in a given area can then be calculated by multiplying the annual release rate by the surface area of the material (Equation 5).

(Equation 5)

$$\text{Annual mass release (kg/yr)} = \text{annual release rate } (\text{mg/m}^2/\text{yr}) \times \text{material area } (\text{m}^2) \times \frac{\text{kg}}{10^6\ \text{mg}}$$

Data Quality

Quality of Laboratory Analyses

Quality of metals and hardness data was assessed through analysis of lab blanks, lab control samples (spiked blanks), and matrix spikes. Analyses were performed in duplicate for each sample batch (≤20 samples) to yield a measure of precision.

Quality of DOC and TSS data was assessed through analysis of a single lab blank, lab control sample, and matrix spike per sample batch. To assess precision, one sample per batch was analyzed in duplicate.

Bias

With few exceptions, metals and conventionals (DOC, TSS, and hardness) were free of measurable laboratory contamination based on analysis of lab blanks. Copper was detected in 2 blanks (0.046 and 0.044 µg/L; Storms 4 and 5, respectively) and zinc was detected in one blank (0.16 µg/L, Storm 5) at or near the method detection limits and are considered insignificant relative to sample results. All blanks analyzed for conventionals were nondetects.

Laboratory control samples for metals and hardness had recoveries of 96%–110%, which are well within the control limits of 85%–115%. Recoveries for DOC and TSS were 94%–102%, within the control limits of 80%–120%.

Hardness and DOC were well within matrix spike control limits of 75%–125%. Matrix spike recoveries for metals were nearly always within the control limits of 75%–125%. One recovery for zinc (Storm 4) was slightly outside control limits (128%), and two others (also Storm 4) were well outside control limits, due to high native zinc concentrations relative to spike amounts. Other zinc sample batches from Storm 4 had good (97%–108%) recovery.

The arithmetic means for all blank spike recoveries and all matrix spike recoveries for metals was 102% and 103%, respectively. Taken together with the individual sample batch analyses, there is no indication of an overall bias in the laboratory data.

Precision

Overall precision of the laboratory data was good, based on analysis of duplicate quality control (QC) samples. For metals, the relative percent difference (RPD, the difference divided by the mean) never exceeded 5% for duplicates of spiked blanks and rarely exceeded 5% for matrix spike duplicates. Only one matrix spike duplicate had a RPD higher than the QC control limit of 20% (Zn from Storm 4, RPD of 23%). Laboratory precision was also good for hardness analysis, with RPDs ≤3% for both blank spike and matrix spike analyses.

Duplicate sample analysis, rather than duplicate QC sample analysis, was used to measure laboratory precision of DOC and TSS. These results also indicated a high level of precision, with mean RPDs of 1% and 5% for DOC and TSS, respectively. None of the results exceeded the 20% control limit.

Assessment of Sample Homogeneity and Field Contamination

Sample homogeneity and field contamination were assessed through analysis of field duplicates and equipment blanks, respectively. Field duplicates were analyzed for total and dissolved copper and zinc only; conventional parameters were not analyzed.

Sample Homogeneity

Field duplicate samples were collected from two sites for each storm event in order to assess homogeneity of the samples. It should be noted that environmental variability cannot be assessed from these field duplicates, because they are aliquots sampled from the same bulk composite (contained in the buckets, barrels, and roof pools) rather than sampling repeated prior to accumulation of a bulk composite.

Overall, it appears that samples were fairly homogenous, with a few exceptions. The mean RPD for all field duplicates was 13%. However, differences for duplicates sampled from roof pools were much higher (26% overall), likely due to solids that were resuspended when these pools were agitated by stirring. RPDs for total metals at these locations averaged 43%, versus 9% for dissolved metals. When samples from roof pools were removed from the field duplicate data set, the mean RPD was 8%. It is noteworthy that differences in metals concentrations between duplicate samples incorporate laboratory variability as well as sample homogeneity. Although these sources of variability cannot be parsed, they all contribute to overall variability.

Field and Equipment Blanks

Field blanks were used to assess possible contamination during sampling, storage, and transport. Generally, field blanks were obtained by transferring MEL-supplied distilled/deionized water into the sampling containers. Total copper was present in field blanks in four of seven samples, with an average concentration of 0.22 µg/L. In general, total copper in blanks was present at levels <1% of associated washoff samples, except at the O'Brien Building (OBRI) Storm 5 blank, which had total copper at approximately 7% of the washoff sample concentrations. Total zinc was not detected in any of the field blanks.

Filter blank samples consisted of laboratory-supplied distilled/deionized water filtered through a clean Nalgene 0.45-µm filter apparatus (the same type used to filter dissolved metals samples). Most (five of seven) did not have detectable dissolved copper concentrations or had detections below the reporting limit (0.1 µg/L). But for two samples, copper was detected at 0.14 µg/L and 0.4 µg/L. These are relatively high values compared to their associated washoff samples (0.19 µg/L and 1.36 µg/L, respectively). Dissolved zinc was regularly detected in filter blanks (six of seven samples), at an average concentration (1.2 µg/L) slightly above the reporting limit (1.0 µg/L). Since zinc was not detected in any of the nonfiltered field blanks, this suggests that the filter apparatus is a consistent low-level source of zinc contamination.

No method was adopted for blank-correcting or dismissing sample results based on field or filter blanks. In general, metals contamination stemming from handling, storage, or filtering appeared to contribute little to the concentrations found in washoff samples.

Equipment blanks were analyzed for the atmospheric deposition devices during each round of sampling, except Storm 1. Laboratory-supplied distilled/deionized water was used to rinse the decontaminated collection funnel and MPTFE liner and subsequently analyzed for total and dissolved metals.

The atmospheric deposition equipment blanks contained substantial concentrations of both copper and zinc. Copper and zinc in blanks averaged 3.8 µg/L and 6.6 µg/L, respectively. More importantly, copper in blanks was 52% of the sample concentration on average, and zinc was 81% on average. The high concentrations of metals in atmospheric blank samples has significant implications for interpretation of the atmospheric deposition results. They are discussed in more detail in the *Results* section of this report.

Results

Complete results for each location can be found in Appendix C.

Evaluation of Sampling Success

Sampling success was good overall, but a number of limitations precluded obtaining all of the samples as planned. The Quality Assurance Project Plan (QAPP) for this research (Bookter, 2017b) called for sampling of all materials during six separate storm events, but the late start to sampling (mid-February), the labor demands in preparing for storms (two to three days, requiring two to four staff), difficulty in anticipating qualifying storms, and other logistical problems (e.g., coordinating with building managers to obtain roof access) allowed for only five complete sampling events before the dry summer season set in. Sampling was conducted during a sixth storm event (Storm 2.5), but it was limited to siding materials.

In general, washoff was collected in sufficient quantity for laboratory analysis of all parameters during all storms. Insufficient sample volume occurred during the following instances:

- One ethylene propylene diene terpolymer (EPDM) sample was not collected, due to a leak in the rooftop dam assembly.
- One light standard and two chain-link fence samples were not collected, due to small sample volumes. In other instances, sample volumes were too small to conduct analysis for dissolved metals or conventional parameters.
- Collecting sufficient volume for siding materials proved especially problematic. For the different siding types, the sampling success was as follows:
    - painted fiber cement (SFBR) = 56%
    - metal less than 5 years old (SMT<5) = 78%
    - metal greater than 10 years old (SMT>10) = 72%
    - painted wood (SWD) = 17%

  In a number of cases, sample volumes were sufficient only for total copper and zinc analysis, and dissolved metals could not be analyzed. Only occasionally was volume sufficient for analysis of conventional parameters. Low sample volumes were due to lack of wind-driven rain and roof overhangs that prevented siding from being exposed to the rain. The artificial rainwater washoff effort was conducted to augment the siding data and is addressed separately from the storm washoff results.

Conventional Parameters

Tables 5 and 6 summarize conventional parameters measured in the field and at MEL. Median concentrations of conventional parameters among material types were generally similar. Few samples had outlier results. One exception is a sample from NEIL-RAAR (RAAR>10; Appendices A, C), which had the lowest pH among all samples, and the highest conductivity, turbidity, and DOC among samples from building components. Field observations noted that this sample was a brownish color and very turbid; it may have been influenced by nearby overhanging trees.

A single sample from the PNR-CNLNK location (Appendices A, C) had particularly high specific conductance, and this sample also had high DOC and hardness. Since it was the only sample analyzed from this location due to consistently small sample volumes, it is impossible to assess the representativeness of the results. Field observations indicate that this sample might have been influenced by debris from nearby trees. Results from other chain-link samples have conventional parameter results more typical of other material types.

Table 5. Summary of results for field-measured conventional parameters in washoff water.

Material type	*n*	**pH**			**Specific conductance (µS/cm)**			**Temperature (°C)**			**Turbidity (NTU)**		
		Min	*Median*	*Max*	*Min*	*Median*	*Max*	*Min*	*Median*	*Max*	*Min*	*Median*	*Max*
ATM	3	5.65	6.32	7.51	3.5	9.2	9.3	5.98	11.2	12.8	0.8	1.7	1.8
CNLNK	1	--	7.44	--	--	5,500	--	--	19.2	--	--	26	--
GUTT	15	5.37	5.92	6.60	4.7	7.8	49	3.84	13.3	21.1	0.5	1.0	16
LGT	8	6.55	6.88	7.10	32	46	71	3.66	11.2	20.4	0.6	1.8	9.8
RAAR<5	15	5.32	6.42	7.54	6.3	22	85	4.12	13.7	22.1	0.7	1.8	15
RAAR>10	15	4.85	6.81	7.41	23	33	167	4.14	10.8	15.6	0.7	1.5	1,200
REPDM	14	5.30	6.06	7.64	9.3	25	76	3.05	13.5	34.5	0.6	2.4	18
RMT<5	14	5.29	6.05	6.94	0.20	74	22	4.27	14.0	18.1	0.8	1.6	15
RMT>10	15	5.80	6.21	6.85	2.4	9.1	45	3.99	10.5	15.7	0.7	1.8	50
RTPO	12	5.92	6.38	7.30	2.8	11	31	3.65	15.6	28.5	0.6	1.4	7.0
SFBR	1	--	7.62	--	--	16	--	--	9.41	--	--	5.0	--
SMT<5	1	--	6.50	--	--	9.6	--	--	21.6	--	--	3.4	--
SMT>10	1	--	7.05	--	--	24	--	--	14.4	--	--	3.2	--

Table 6. Summary of results for laboratory-measured conventional parameters in washoff water.

Material type	**Hardness as $CaCO_3$ (mg/L)**				**Dissolved organic carbon (mg/L)**				**Total suspended solids (mg/L)**			
	n	*Min*	*Median*	*Max*	*n*	*Min*	*Median*	*Max*	*n*	*Min*	*Median*	*Max*
ATM	9	0.30	0.51	2.2	8	0.5	0.83	11	7	2	7	160
CNLNK	6	0.91	2.4	130	2	6.2	790	1,600	0	--	--	--
GUTT	15	0.51	1.3	2.9	15	0.5	3.9	49	15	1	2	56
LGT	14	0.53	1.4	3.6	14	1.8	5.2	14	12	2	8	43
RAAR<5	15	2.0	8.6	27	15	1.1	10	82	15	1	5	67
RAAR>10	15	9.8	14	31	15	2.5	10	200	15	1	5	55
REPDM	14	0.36	3.5	12	14	1.4	17	83	14	1	18	140
RMT<5	14	0.54	1.5	4.9	14	0.5	2.7	22	14	2	7	32
RMT>10	15	0.58	1.4	24	15	0.5	4.2	120	15	1	5	170
RTPO	14	0.59	3.3	9.1	14	0.5	6.3	46	14	1	14	150
SFBR	2	0.84	1.3	1.8	2	0.8	1.4	2.1	1	4	4	4
SMT<5	5	1.1	2.4	28	3	1.9	2.1	2.8	3	6	8	120
SMT>10	6	0.74	2.1	4.9	5	1.2	2.8	18	3	3	8	25

Copper Concentrations in Washoff Water

Total copper was detected in all washoff samples analyzed (*n* = 171). Dissolved copper was also detected in all samples analyzed, but these numbered 14% fewer (*n* = 145) than total copper due to insufficient aliquot volumes in some instances. Table 7 summarizes results sorted by material type. Boxplots showing total copper and dissolved copper concentrations for all material types except RAAR<5 are shown in Figure 13. RAAR<5 samples are omitted from Figure 13 due to their elevated values and are treated separately.

RAAR<5 aside, median total copper concentrations were less than 8 µg/L and dissolved copper concentrations were less than 6 µg/L for all materials analyzed. Mean concentrations for both total copper and dissolved copper were higher than median values due to positively skewed distributions. Dissolved copper concentrations were approximately 60% of total copper concentrations on average, although in one case (SMT<5) mean dissolved and total copper concentrations were the same.

By far the highest copper concentrations were from RAAR<5 washoff. Median total and dissolved copper concentrations were one to two orders of magnitude higher than concentrations from most other material types. Concentrations of total and dissolved copper at the three RAAR<5 locations were typically greater than 100 µg/L and were highest during Storms 3 and 4, which had the lowest precipitation amounts (Figure 14). For all of the roof and gutter materials sampled, copper concentrations were generally highest during Storms 3 and 4. This is consistent with findings by He (2002), who observed an inverse relationship between storm intensity and metals runoff in various roof materials. However, the highest precipitation events did not necessarily lead to the lowest concentrations. Copper concentrations at RAAR>10 locations were not nearly as high as those at RAAR<5 locations, but were generally higher than other roofing material types.

Table 7. Summary of results for copper in washoff water from all material types.

Material category	**Material type**	**Total copper (µg/L)**					**Dissolved copper (µg/L)**				
		n	*Min*	*Median*	*Mean*	*Max*	*n*	*Min*	*Median*	*Mean*	*Max*
Roofing and gutter	RAAR<5	15	18	134	436	2,170	15	17	110	376	1,950
	RAAR>10	15	1.8	6.2	17	136	15	1.3	5.0	7.7	19
	REPDM	14	1.2	4.9	5.6	14	14	0.35	2.5	3.8	13
	RMT<5	15	0.70	1.6	2.4	11	14	0.37	0.79	1.2	3.0
	RMT>10	15	0.28	1.2	2.1	7.9	15	0.16	0.72	0.85	3.3
	RTPO	15	0.22	2.0	4.2	20	15	0.09	1.1	2.4	10
	GUTT	15	0.38	1.5	1.7	4.0	15	0.24	0.95	1.3	3.6
Siding	SFBR<5	10	0.26	2.9	13	90	6	0.10	1.3	1.9	4.4
	SMT<5	14	0.69	4.5	11	44	7	0.69	1.8	11	39
	SMT>10	13	0.85	4.9	6.0	17	6	0.50	0.93	1.9	4.3
	SWD>10	3	5.0	7.2	11	21	1	6.0	6.0	6.0	6.0
Other	CNLNK	13	0.55	3.4	7.5	25	8	0.38	1.6	3.2	11
	LGT	14	1.4	4.2	4.5	9.1	14	0.80	2.6	2.8	5.6

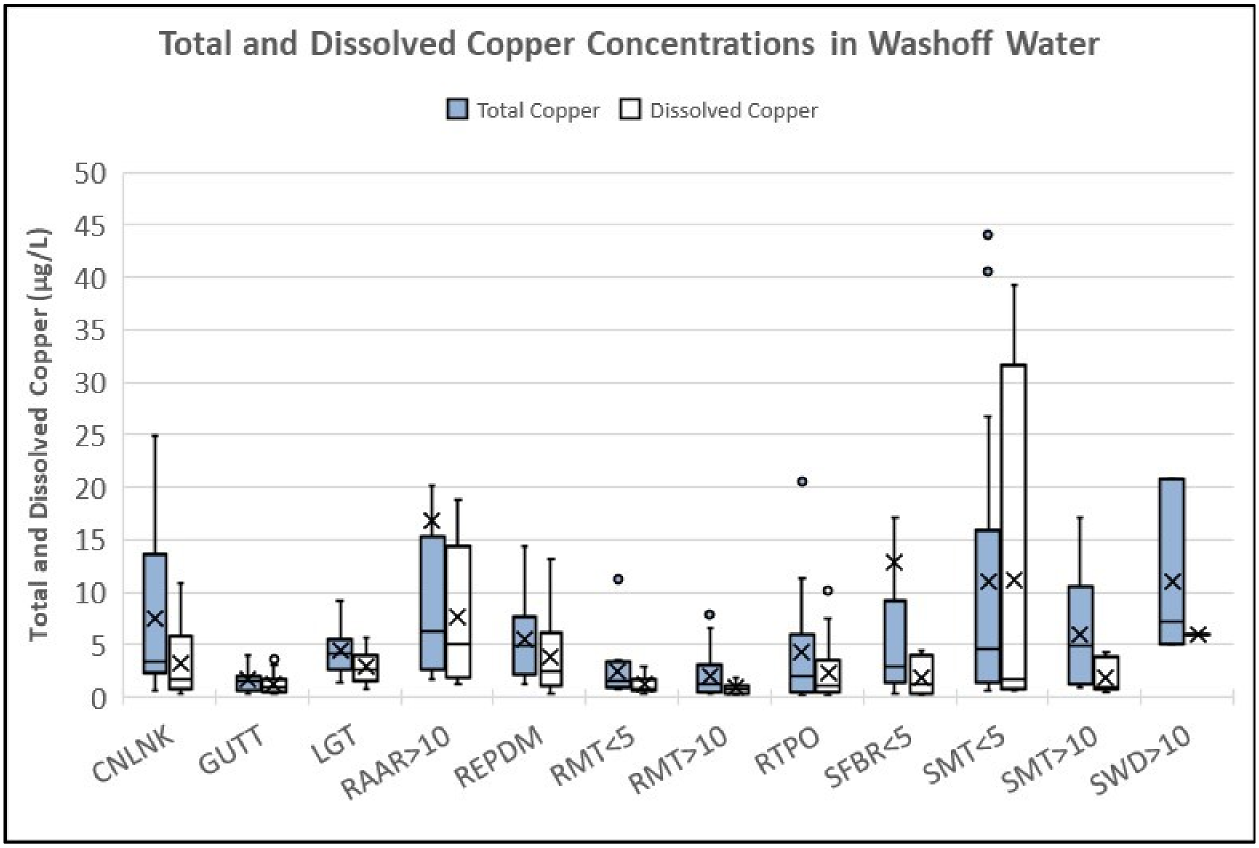

Figure 13. Total and dissolved copper concentrations in washoff water for all material types except asphalt shingles with algae-resistant granules less than 5 years old (RAAR<5). Outlier values not shown here are 136 µg/L for RAAR>10 and 90 µg/L for SFBR<5. See Table 4 for material type abbreviations.

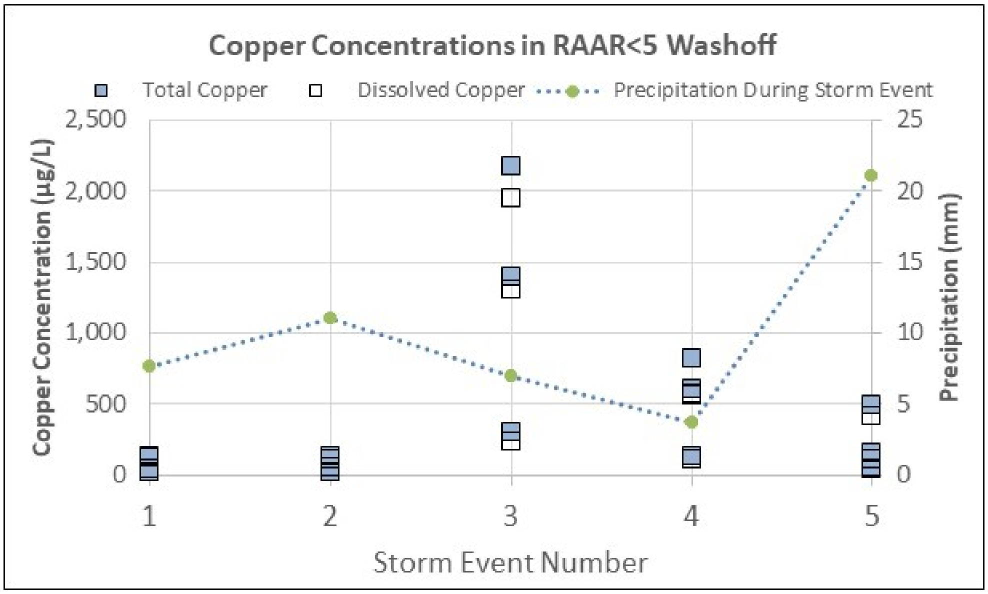

Figure 14. Copper concentrations in washoff from asphalt shingles with algae-resistant granules less than 5 years old (RAAR<5) during the five storm events.

Copper concentrations in gutter washoff were generally low compared to other materials. Median concentrations in gutter washoff for total and dissolved copper were 1.5 and 0.95 µg/L, respectively. Figure 15 shows concentrations of total and dissolved copper in metal roofs and their companion gutters for each storm event. Gutters appear to contribute some enrichment of total copper to washoff from the metal roofs on which they were paired. On average, total copper in gutters was 14% higher than their companion roofs when compared on a storm-by-storm basis. Dissolved copper was more consistently higher (mean of 35% higher) in gutters than in their companion roofs. The newest roof/gutter combination (1 year old) at the MECO location had the highest concentrations of both total and dissolved copper, but there does not appear to be an overall trend related to the age of the roof and gutter materials.

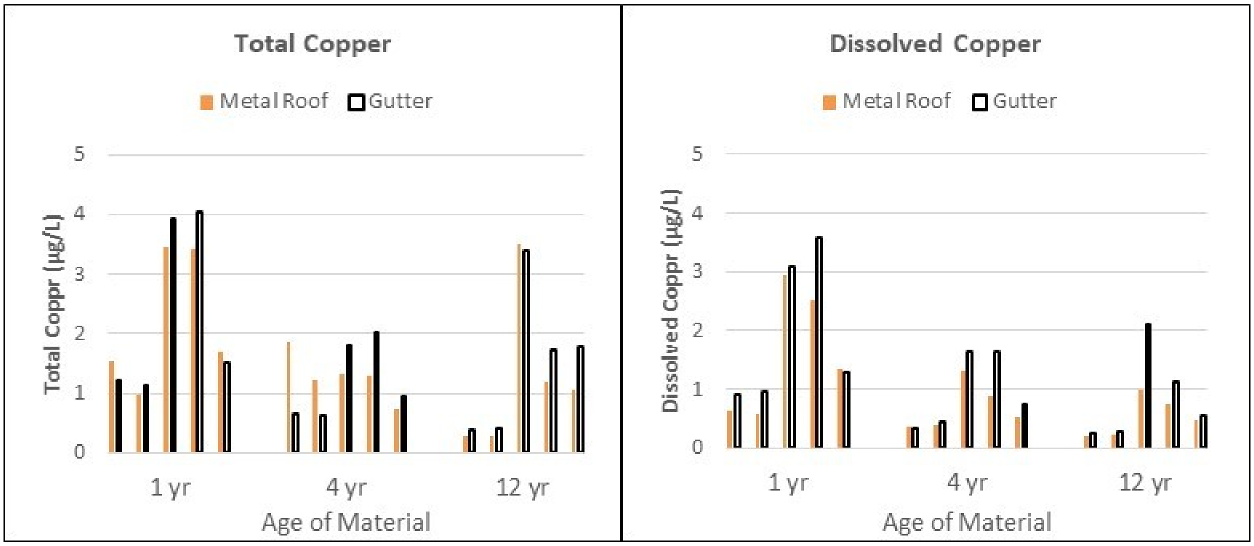

Figure 15. Copper concentrations in metal roof and companion gutter washoff for each storm event. Roof and gutter materials are clustered by age of materials. —*Left*, total copper. —*Right*, dissolved copper.

Zinc Concentrations in Washoff Water

Total zinc was detected in all washoff samples analyzed (*n* = 171). Dissolved zinc was also detected in all samples analyzed, but these numbered 14% fewer (*n* = 145) than total zinc samples due to insufficient aliquot volumes in some instances. Table 8 shows a summary of results sorted by material type. Boxplots showing total and dissolved zinc concentrations for all material types except chain-link fencing (CNLNK) and light standards (LGT) are shown in Figure 16. CNLNK and LGT samples are omitted due to their elevated values and are treated separately.

CNLNK and LGT aside, median total and dissolved zinc concentrations were less than 300 µg/L. Mean concentrations for both total and dissolved zinc were higher than median values due to positively skewed distributions. Dissolved zinc concentrations were approximately 90% of total zinc concentrations on average, but for fiber cement siding (SFBR) and older metal siding (SMT>10), median dissolved zinc was higher than median total zinc concentrations.

Among the roofing materials tested, metal roofing materials were higher on average than non-metal roofing. One older metal roofing (RMT>10) location (SAND-RMT) had particularly high zinc concentrations, at or above 1,000 µg/L during all storm events. These results drastically skewed the distribution of this material type, as shown in Figure 16. Siding materials had mean zinc concentrations greater than roofing materials (except RMT>10).

Table 8. Summary of results for zinc in washoff water from all material types.

Material category	**Material type**	**Total Zn (µg/L)**					**Dissolved Zn (µg/L)**				
		n	*Min*	*Median*	*Mean*	*Max*	*n*	*Min*	*Median*	*Mean*	*Max*
Roofing and gutter	RAAR<5	15	3.8	13	21	94	15	2.9	8.7	18	83
	RAAR>10	15	7.1	38	69	418	15	6.7	34	44	111
	REPDM	14	26	147	147	268	14	12	132	136	250
	RMT<5	15	15	31	165	696	14	12	18	119	458
	RMT>10	15	8.5	32	804	6,240	15	8.5	25	738	6,360
	RTPO	15	2.2	16	39	277	15	2.2	14	15	42
	GUTT	15	14	28	37	80	15	14	27	33	68
Siding	SFBR<5	10	4.2	188	413	1,760	6	27	231	495	1,730
	SMT<5	14	46	147	254	1,040	7	44	107	253	864
	SMT>10	13	12	99	333	2,040	6	10	292	293	599
	SWD>10	3	56	274	223	338	1	249	249	249	249
Other	CNLNK	13	3,880	7,700	10,360	21,800	8	3,470	7,405	8,050	14,100
	LGT	14	7,680	11,050	12,520	22,500	14	7,800	10,505	12,320	22,900

Zinc concentrations in gutter washoff were generally low compared to other materials. Median concentrations in gutter washoff for total and dissolved zinc were 28 and 27 µg/L, respectively. Figure 17 shows concentrations of total and dissolved zinc in metal roofs and their companion gutters for each storm event. Gutters appear to substantially enrich both total and dissolved zinc washed off of their companion roofs. On average, total zinc in gutters was 89% higher and dissolved zinc was 114% higher than their companion roofs when compared on a storm-by-storm basis. Both total and dissolved zinc were generally higher in the newer (1-year-old) roof and gutter washoff at the MECO location compared to both the 4-year-old or 12-year-old roofs and gutters.

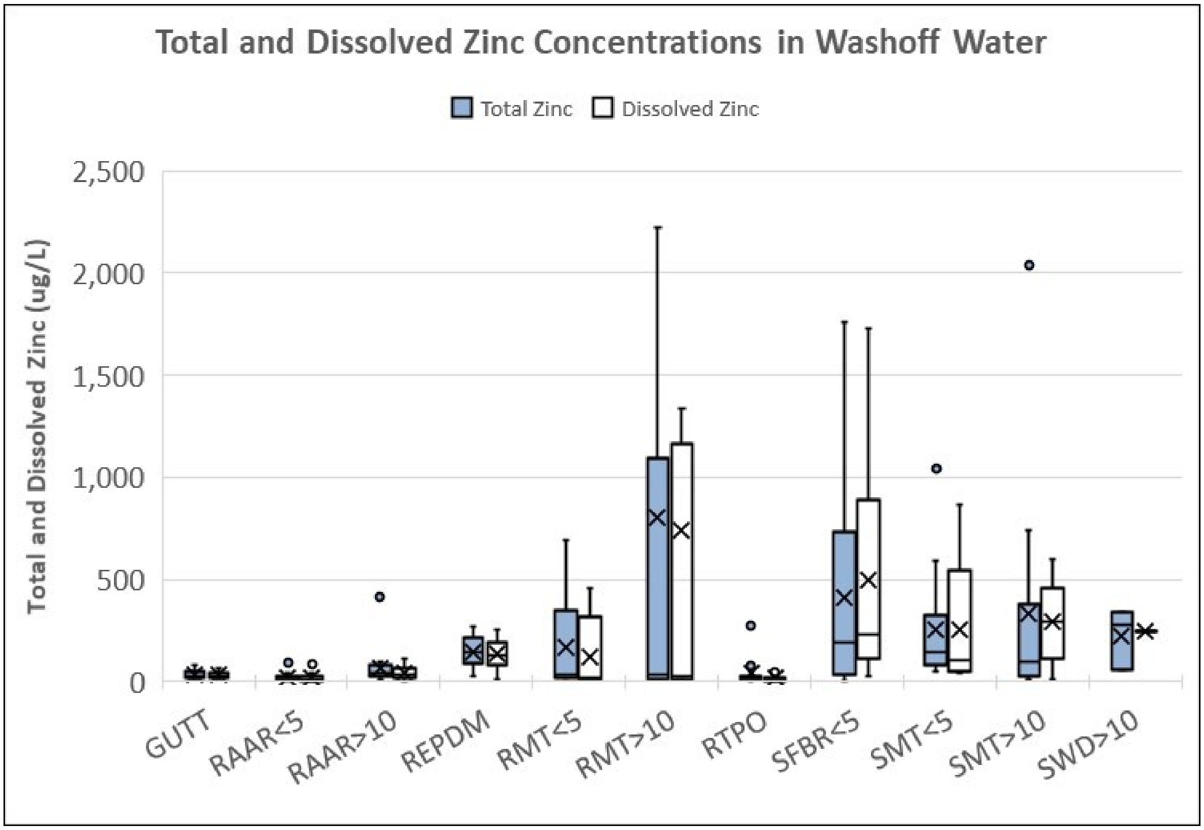

Figure 16. Total and dissolved zinc concentrations in washoff water for all material types except chain-link fencing (CNLNK) and light standards (LGT). Outlier values not presented here are 6,360 µg/L and 6,240 µg/L for RMT>10. See Table 4 for material type abbreviations.

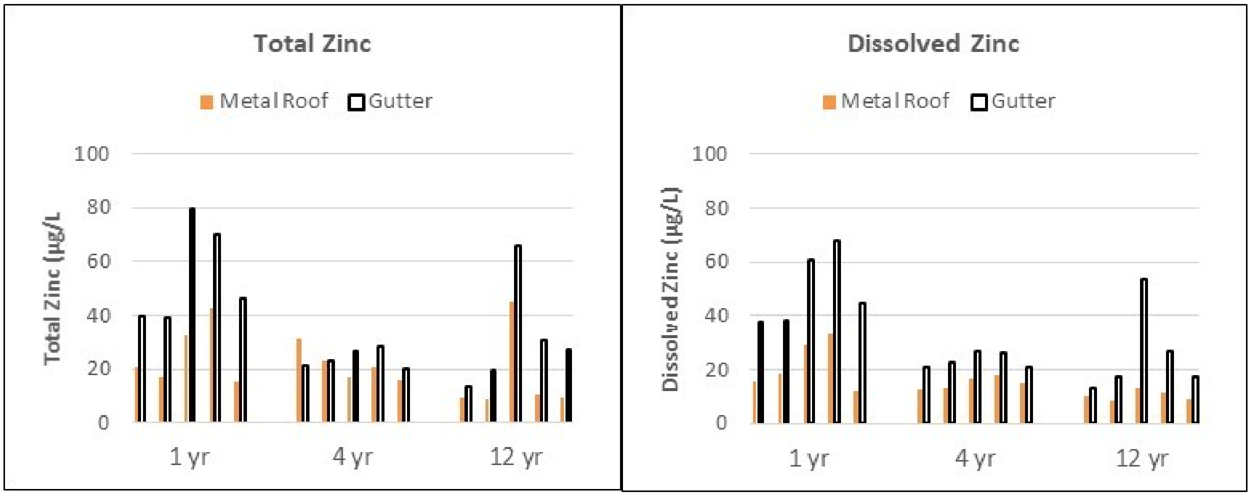

Figure 17. Zinc concentrations in metal roof and companion gutter washoff for each storm event. Roof and gutter materials are clustered by age of materials. —*Left*, total zinc. —*Right*, dissolved zinc.

Washoff from exposed galvanized materials — CNLNK and LGT — had the highest zinc concentrations by far. Mean zinc concentrations in CNLNK and LGT washoff were at least one to two orders of magnitude higher than those from other materials (Figure 18). Aside from small sections of exposed flashing and perhaps fasteners, these were the only materials sampled that had large areas of exposed galvanized metals.

Results from materials with the highest zinc concentrations suggest that older materials release more zinc in washoff than newer materials. LGT, RMT>10, and SMT>10 materials were up to 30 years old, and washoff from these older materials were consistently higher than newer materials for each type (Figure 19). Age of CNLNK sampled spanned only 4 years (7 to 11 years) and concentrations did not appear to differ appreciably with age.

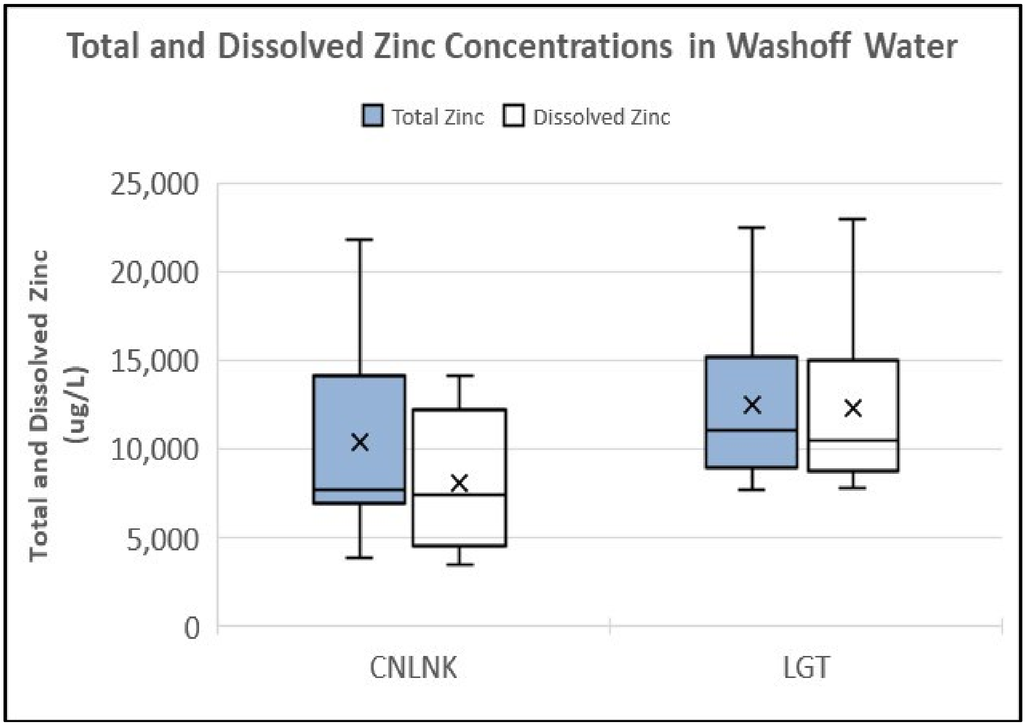

Figure 18. Boxplots showing total and dissolved zinc concentrations in washoff for chain-link fencing (CNLNK) and light standards (LGT).

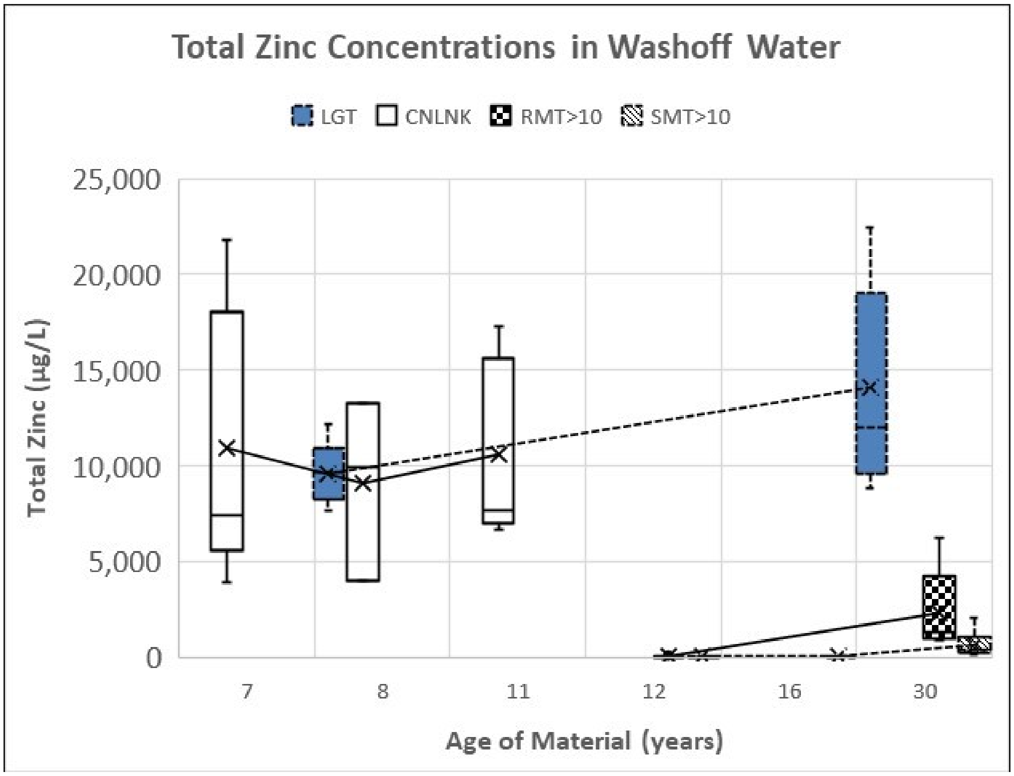

Figure 19. Boxplots showing total zinc concentrations in washoff from different ages of light standards (LGT), chain-link fencing (CNLNK), older metal roofing (RMT>10), and older metal siding (SMT>10). Lines connect the means of each material type.

Copper and Zinc Concentrations in Atmospheric Deposition

Bulk atmospheric deposition samples (i.e., dry + wet deposition) were collected in order to account for aerially deposited copper and zinc, particularly as a gauge of contributions to roof washoff. Results show copper concentrations in atmospheric deposition samples elevated well above those in building material washoff samples, whereas zinc concentrations are more comparable to those found in washoff (Figure 20).

The comparatively high copper concentrations in atmospheric deposition samples are puzzling. Concentrations were particularly high (≥200 µg/L) during the first storm event at both of the locations where samplers were deployed. Copper concentrations decreased substantially during subsequent storm events and were <3 µg/L during the final sample collection. Since copper concentrations at both locations followed the same pattern, it is unlikely that localized copper sources were the reason for the elevated levels. A more plausible explanation is that sampling equipment was the source of copper enrichment.

Atmospheric deposition collection funnels were fabricated by welding together stainless steel bowls and funnels. While not verified, the suspicion is that these exposed welds might have leached copper. In addition, fresh welds would likely leach more copper than weathered welds, explaining higher copper in initial samples. The atmospheric deposition equipment blanks contained substantial concentrations of both copper and zinc as discussed in the Data Quality section, lending weight to the notion that sampling equipment was the source of elevated concentrations. Due to the uncertainty around copper and zinc in atmospheric deposition, the data are not used in further evaluation of washoff from building materials.

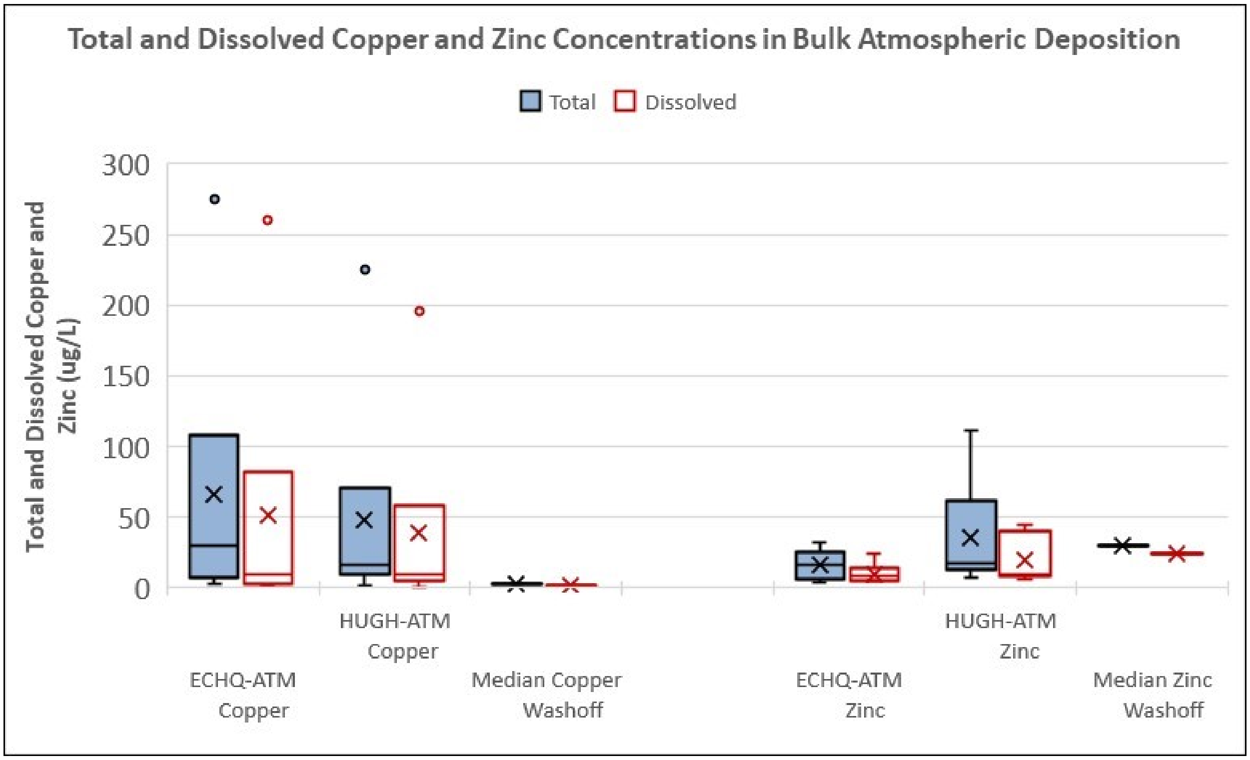

Figure 20. Boxplots of total and dissolved copper and zinc concentrations in bulk atmospheric deposition samples. Median copper and zinc concentrations for all roof and gutter washoff samples are shown for comparison. See Appendix A for sample site information.

Copper and Zinc Concentrations in Siding Washoff Using Artificial Rainwater

Artificial rainwater washoff sampling was conducted in August 2018 to supplement data on copper and zinc in siding washoff. Samples were collected from washoff generated by applying a known volume of artificial rainwater to a controlled area of siding material.

The overall median total copper in washoff using artificial rain was low (1.1 µg/L), about four times lower than the overall mean of total copper in siding washoff generated during storms (4.7 µg/L). Dissolved copper concentrations composed about one-half of total concentrations on average, with a median of 0.6 µg/L. The percent contribution of dissolved copper to total copper was similar to that of storm washoff from siding. Among material types, wood siding (SWD) had the highest mean copper concentrations, followed by fiber cement siding (SFBR) and metal siding (SMT) (Table 9).

The overall median total zinc concentration in artificial rain washoff (30 µg/L) was approximately one-fifth of that from siding washoff in storms (170 µg/L). Dissolved zinc composed about 90% of total on average, with an overall median of 30 µg/L. The percent contribution of dissolved zinc to total zinc was similar to that of storm washoff from siding. Mean zinc in SWD was one to two orders of magnitude higher than SFBR and SMT.

Table 9. Summary of results for copper (Cu) and zinc (Zn) in siding washoff generated using artificial rainwater.

Material type	**Total Cu (µg/L)**		**Dissolved Cu (µg/L)**		**Total Zn (µg/L)**		**Dissolved Zn (µg/L)**	
Siding	*n*	*Mean*	*n*	*Mean*	*n*	*Mean*	*n*	*Mean*
SFBR	6	2.3	6	1.1	6	68	6	63
SMT<5	4	0.91	4	0.37	4	29	4	23
SMT>10	2	1.4	2	1.0	2	3.8	2	3.6
SWD	6	6.8	6	2.3	6	1,700	6	1,500

At locations where both artificial rain and storm washoff samples were collected, total copper concentrations were 70%–90% lower than storm-generated concentrations, except at one location (EAGL-SFBR; see Appendix A) where concentrations were nearly identical (Figure 21). Total zinc concentrations were 30%–90% lower in artificial rainwater washoff, again the exception being EAGL-SFBR. Zinc concentrations in artificial rainwater at this location were more than double those from storm-generated washoff (Figure 22).

The CAC location (see Appendix A) had exceptionally high concentrations of zinc in artificial washoff samples and has a large influence on the resulting mean calculated for SWD. This location produced only a small amount of washoff during storm events — a maximum of 30 mL — and never produced adequate volumes for metals analysis. Although the sampling location was oriented toward the prevailing wind on the southwest side of the building, the siding received little precipitation exposure, likely due to tree cover. As a result, dust and dirt was able to build up on the siding and consequently washed off during application of the artificial rainwater. Samples from CAC-SWD had noticeably high content of particulate matter, and it appears that elevated zinc values, and copper to a lesser extent, were due to the particles washed off of this siding.

Elevated levels of copper and zinc resulting from dirt and dust particles in siding washoff does not appear to be limited to the CAC location, although the CAC location is an extreme situation. Sampling of siding washoff using artificial rainwater consisted of two sequential rinses of the target (0.5 m^2) siding, with samples collected after each rinse. In all but one case, copper and zinc concentrations were higher in washoff from the first rinse compared to the second rinse. Respective concentrations for total and dissolved copper were 60% and 59% higher in the first rinse on average. For total and dissolved zinc, mean concentrations in the first rinse were 52% and 41% higher, respectively. As a percent of total, dissolved copper and dissolved zinc concentrations were higher in the second rinse samples, perhaps suggesting that more metals were bound to particulate matter that was washed off during the first rinse.

This first-rinse effect does not fully explain differences between metals concentrations found during storm events and artificial rainwater washoff. Total copper and total zinc concentrations in artificial rainwater washoff are typically 60%–80% lower than those in storm washoff, even when only first-rinse artificial washoff samples are used for the comparisons (except for the EAGL location).

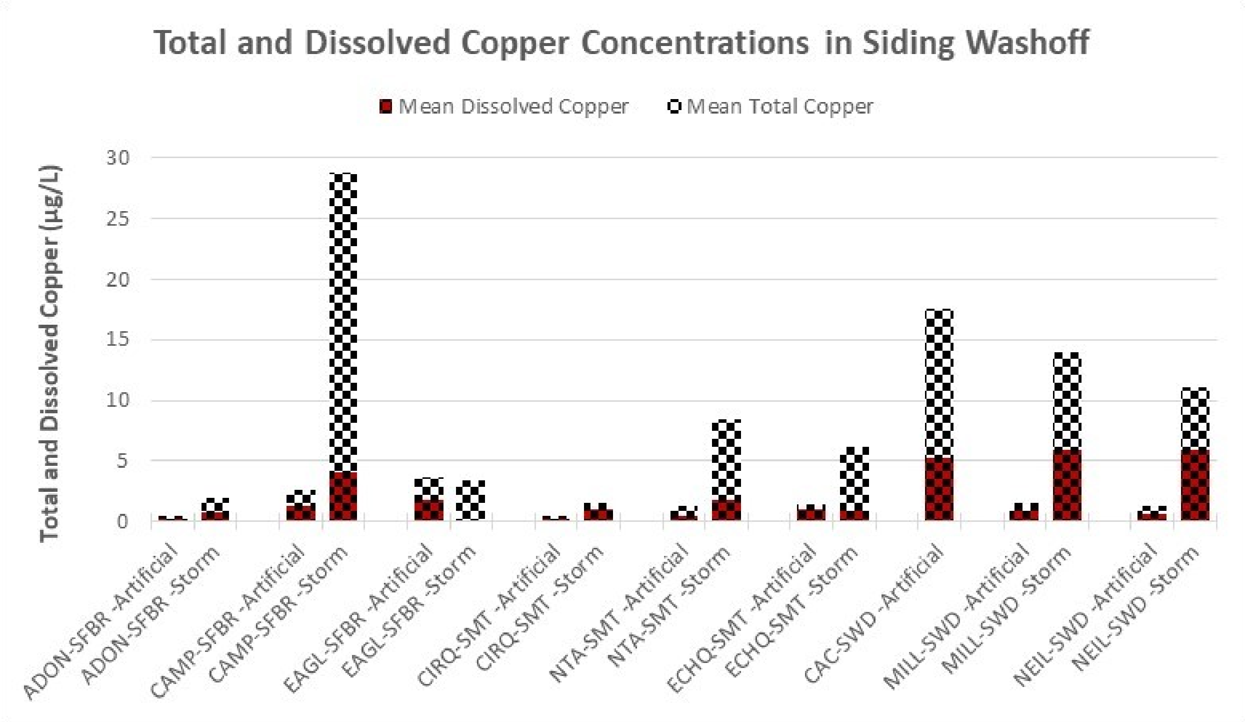

Figure 21. Site-by-site comparisons of total and dissolved copper concentrations in siding washoff from artificial rainwater and natural storms. See Appendix A for site and material information.

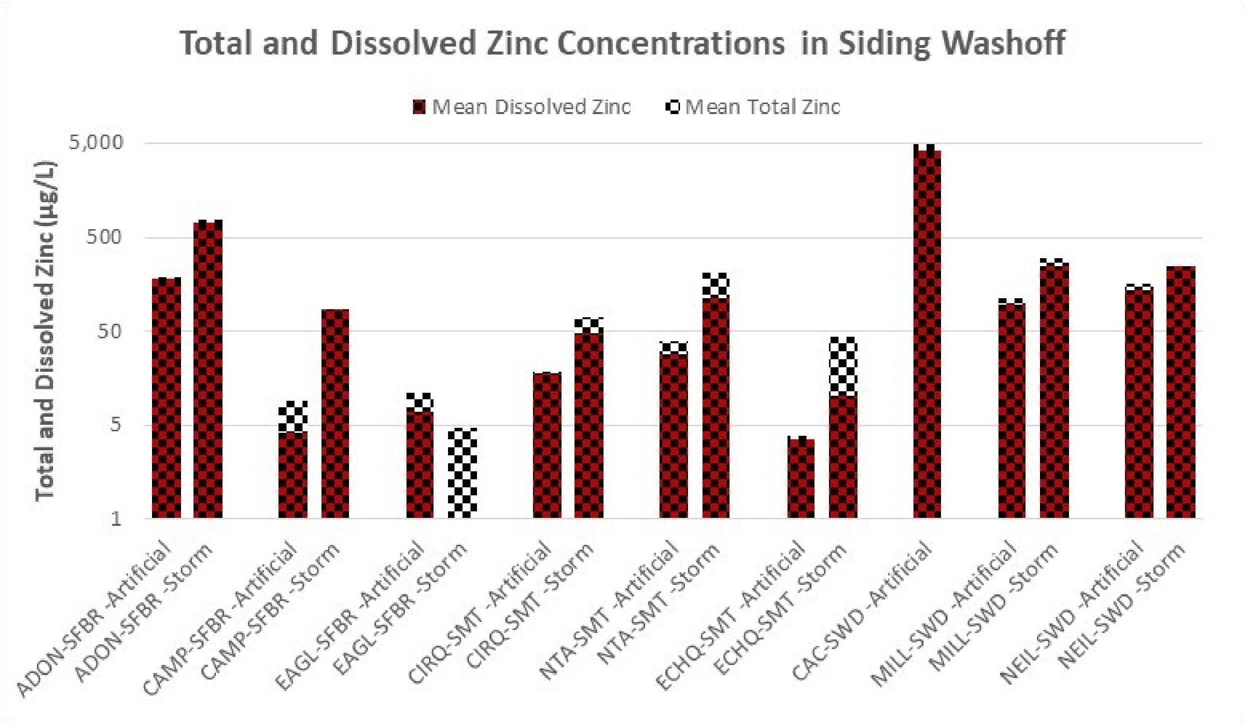

Figure 22. Site-by-site comparisons of total and dissolved zinc concentrations in siding washoff from artificial rainwater and natural storms. Note logarithmic scale on y-axis. See Appendix A for site and material information.

Discussion

Copper and Zinc in Roof Washoff and Effects of Atmospheric Deposition

Estimating large-scale copper and zinc releases from roofing materials is complex, due to a variety of factors. Chief among them are the variety of roof materials to consider and the need to account for atmospheric deposition. The latter includes copper and zinc contained in rainwater, which affects concentrations in washoff from all materials. However, particulate matter from dry atmospheric deposition, and copper and zinc bound to these particles, has a greater tendency to accumulate on the horizontal or near horizontal surfaces that roofs provide. This accumulation is likely to result in copper and zinc enrichment of roof washoff.

There are several ways to account for copper and zinc from atmospheric deposition. One effective method is to capture washoff from a control panel. If control panels known to be free of copper and zinc are installed near and at the same aspect and slope of the roofs of interest, copper and zinc in the control washoff can simply be subtracted from the roof washoff to account for aerial deposition. This was the approach used successfully in the Ecology Roofing Study, where differences between control and test panels were not significant, suggesting little contribution from atmospheric deposition.

Another approach is to simply collect and analyze bulk atmospheric deposition samples in the general vicinity of the roofs being sampled. This approach was used in the present study (*CuZn Phase 2*) because it did not require installation of a companion control panel on each roof sampled. While more practical, this approach does not allow for teasing out local variations in aerially deposited copper and zinc from suspension of exposed soil, road wear, and local emissions. In the end, however, it appears that elevated copper and zinc in the atmospheric deposition samples analyzed here originated from equipment contamination rather than local sources.

Comparisons with Previous Atmospheric Deposition Studies

Atmospheric deposition sampling for chemicals, including copper and zinc, has been conducted in the Puget Sound area during the past decade. Brandenberger et al. (2010) conducted a year-long monitoring effort to estimate loadings to Puget Sound as part of the Puget Sound Toxics Loading Assessment (PSTLA). One station at the undeveloped Nisqually Reach Nature Center is within 8.5 km (5.25 mi.) of both atmospheric deposition stations for *CuZn Phase 2* and provides a gauge of the local background levels. Median bulk atmospheric deposition fluxes for copper and zinc at this station were calculated to be 0.66 and 3.2 mg/m^2/yr, respectively (Figures 23 and 24). By comparison, *CuZn Phase 2* overall median total copper and total zinc fluxes are 20.9 and 17.7 mg/m^2/yr, respectively.

Since the atmospheric deposition stations for *CuZn Phase 2* were located in commercial areas within 1 km from Interstate 5, some deposition from local sources might be expected. Brandenberger et al. (2010) found the highest flux of copper (4.4 mg/m^2/yr) and zinc (18 mg/m^2/yr) in Tacoma near Interstate 5, and a recent study of bulk atmospheric fluxes in the Duwamish River basin found that in urban residential, commercial, and industrial areas, fluxes of copper (4–9 mg/m^2/yr) and zinc (17–45 mg/m^2/yr) were about five-fold those found in rural and forested areas (King County, 2013).

Calculating release rates of copper and zinc from various construction materials and estimating study area loadings are two of the objectives of *CuZn Phase 2*. Accurate and precise measurement of copper and zinc in atmospheric deposition is required if contributions from atmospheric deposition are to be isolated from release of copper and zinc through leaching and weathering of materials. Results from *CuZn Phase 2* atmospheric deposition sampling are unusually high, presumably from sample contamination. Copper is more problematic than zinc. But the sample design alone may not have been adequate to isolate atmospheric deposition contributions with a high level of confidence, even if sample contamination was not an issue. Therefore, loading values are calculated without correcting for atmospheric deposition.

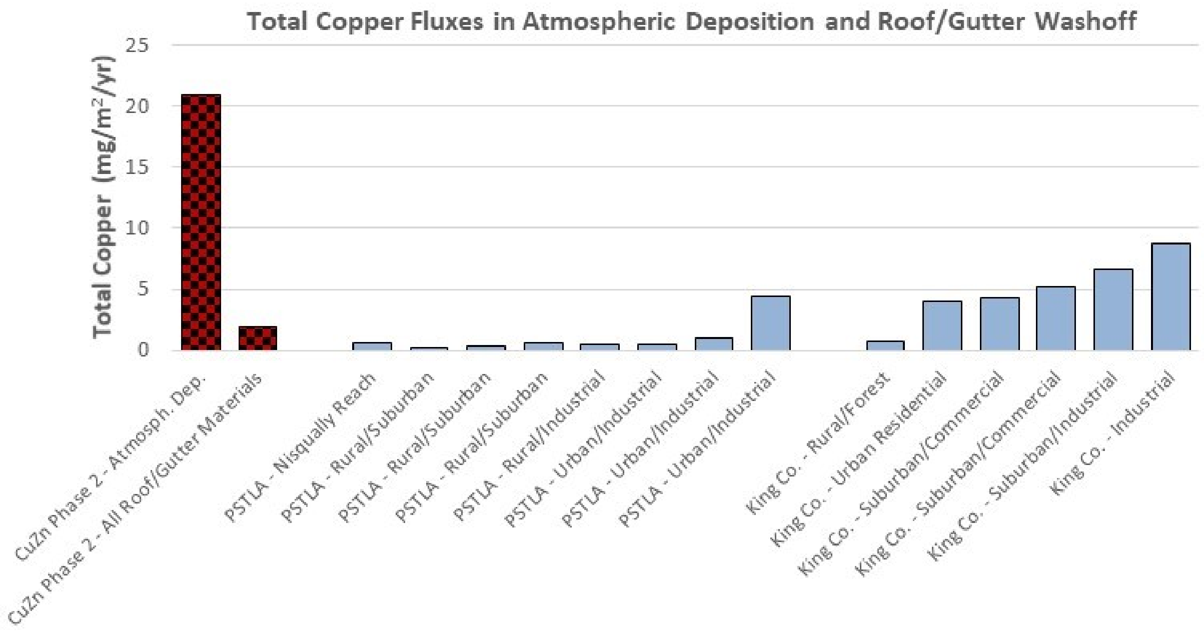

Figure 23. Total copper fluxes measured in atmospheric deposition from *CuZn Phase 2*, Puget Sound Toxics Loading Assessment (PSTLA), and King County. The median unit area release rate for copper in all roof and gutter samples is shown for comparison (“CuZn Phase 2 – All Roof/Gutter Materials”).

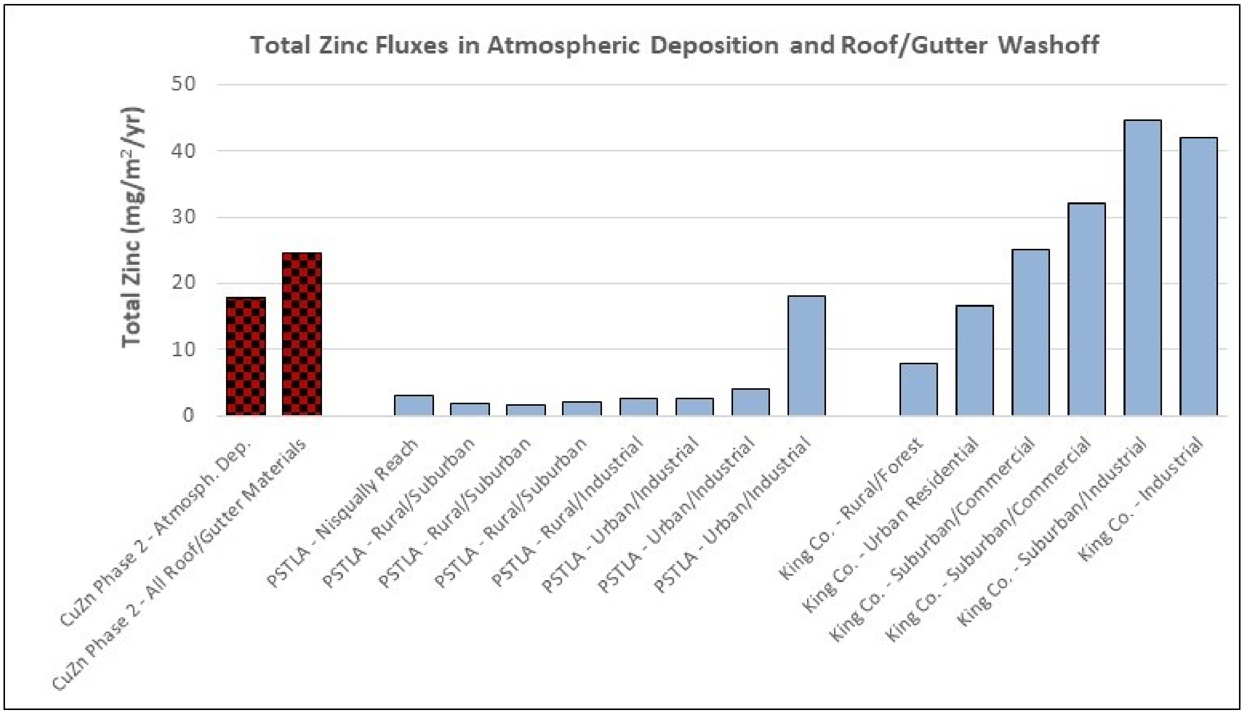

Figure 24. Total zinc fluxes measured in atmospheric deposition from *CuZn Phase 2*, Puget Sound Toxics Loading Assessment (PSTLA), and King County. The median unit area release rate for zinc in all roof and gutter samples are shown for comparison ("CuZn Phase 2 – All Roof/Gutter Materials").

Comparisons with Previous Studies on Roof Washoff

As mentioned previously, one impetus for conducting the *CuZn Phase 2* study was to fill data gaps left by previous studies of roof washoff. For instance, copper and zinc washoff concentrations used to estimate mass loadings in the PSTLA study were based on literature values derived from other regions of the United States and Europe. The Ecology Roofing Study (Winters et al., 2014) sought to generate locally based data, but questions remained about how well they represented washoff in the built environment. *CuZn Phase 2* sought to obtain local data from the built environment in western Washington and thereby fill these information gaps.

To gauge the similarities with previous studies, copper and zinc concentrations in roof washoff from *CuZn Phase 2* were compared with the Ecology Roofing Study, as well as values used to derive mass load estimates in PSTLA and *CuZn Phase 1* (Figures 25 and 26). It should be noted that only *CuZn Phase 2* and the Ecology Roofing Study are exclusively locally derived sampling data, although some of the Roofing Study data were used to calculate median concentrations for *CuZn Phase 1*.

Comparisons suggest that typical copper concentrations in algae-resistant asphalt roof (AAR) washoff differ from those found during the Ecology Roofing Study, and the difference depends on the age of materials. Copper in newer (<5 years) AAR sampled for *CuZn Phase 2* are about five times higher than the AAR washoff from the Ecology Roofing Study, which used new (≤2 years) materials, possibly suggesting differences due to the manufacturer or make of the shingles. Another possibility is that shorter run lengths in the Roofing Study panels resulted in less leaching of metals, as suggested by authors of the study. Neither data set was corrected for effects of atmospheric deposition.

Unfortified asphalt shingle data are also provided for comparison in Figures 25 and 26. Concentrations used to calculate median copper loads for *CuZn Phase 1* and PSTLA are similar in magnitude to *CuZn Phase 2* AAR>10, as well as the Roofing Study (unfortified asphalt shingle was not analyzed in *CuZn Phase 2*). It might be reasonably assumed that algae-resistant roofs greater than 10 years old resemble unfortified asphalt shingle roofs. This suggests that the copper concentrations used to estimate mass loads from asphalt shingle roofs in *CuZn Phase 1* and PSTLA are reasonable estimates.

For metal (MT) and polymer (EDPM and TPO) roofs, copper concentrations for *CuZn Phase 2* were two to ten times higher than the Ecology Roofing Study. Contact time may have played a role for polymer roofs, because samples were ponded anywhere from several hours to several days during *CuZn Phase 2*, whereas rainwater was allowed to run off the experimental panels relatively quickly in the Roofing Study. In all cases, copper concentrations were low.

The PSTLA copper concentration used to calculate the mean release load for metal roofs was two to three orders of magnitude higher than either *CuZn Phase 2* or the Roofing Study. Implications for this are significant, since metal roofs account for more than half of the PSTLA average copper released from roofs. This suggests that PSTLA might have overestimated average copper releases from this material. The lower end of the concentration range used in PSTLA is more in line with the ranges found in *CuZn Phase 2* and the Roofing Study.

Median zinc concentrations in washoff from AAR and polymer roofing materials was about five-fold higher in *CuZn Phase 2* compared with the Roofing Study, although AAR<5 was only about double the concentrations of the AAR from the Roofing Study. Again, contact time and run length may have been factors in these differences, but it is also possible that washoff from *CuZn Phase 2* was in contact with flashing and other galvanized roof components, resulting in higher zinc.

Painted metal roofs sampled for *CuZn Phase 2* typically incorporated painted flashing and fasteners, and therefore would not be expected to contribute excess zinc. This may explain why median zinc concentrations in *CuZn Phase 2* metal roofs were similar to those from the Roofing Study. However, the range in zinc concentration from metal roofs sampled for *CuZn Phase 2*, especially the older roofs, spanned three orders of magnitude. This suggests that zinc releases from older painted metal roofs may vary substantially based on roof condition.

Perhaps the most important conclusion that can be drawn from these comparisons is that the PSTLA study appears to have vastly overestimated mass zinc releases from roofing. This is worth note because results of the PSTLA study were, to a large extent, the original motivation for conducting the Ecology Roofing Study and the *CuZn Phase 1* and *Phase 2* studies.

The large estimates for zinc releases in PSTLA are due to the high zinc concentrations in washoff used to derive these estimates. Typical zinc washoff concentrations were about two orders of magnitude lower in asphalt and metal roofs sampled during *CuZn Phase 2* compared to PSTLA. Authors of the Roofing Study found similar results but were wary of concluding that PSTLA overestimated zinc concentrations, because their sampling did not fully represent the built environment. The conclusion that PSTLA likely used unrepresentative zinc concentrations for asphalt composite and metal roofs is particularly important. These roof types were estimated to contribute about 70% of the zinc releases from all roofs and about 60% of the total zinc releases in the Puget Sound basin.

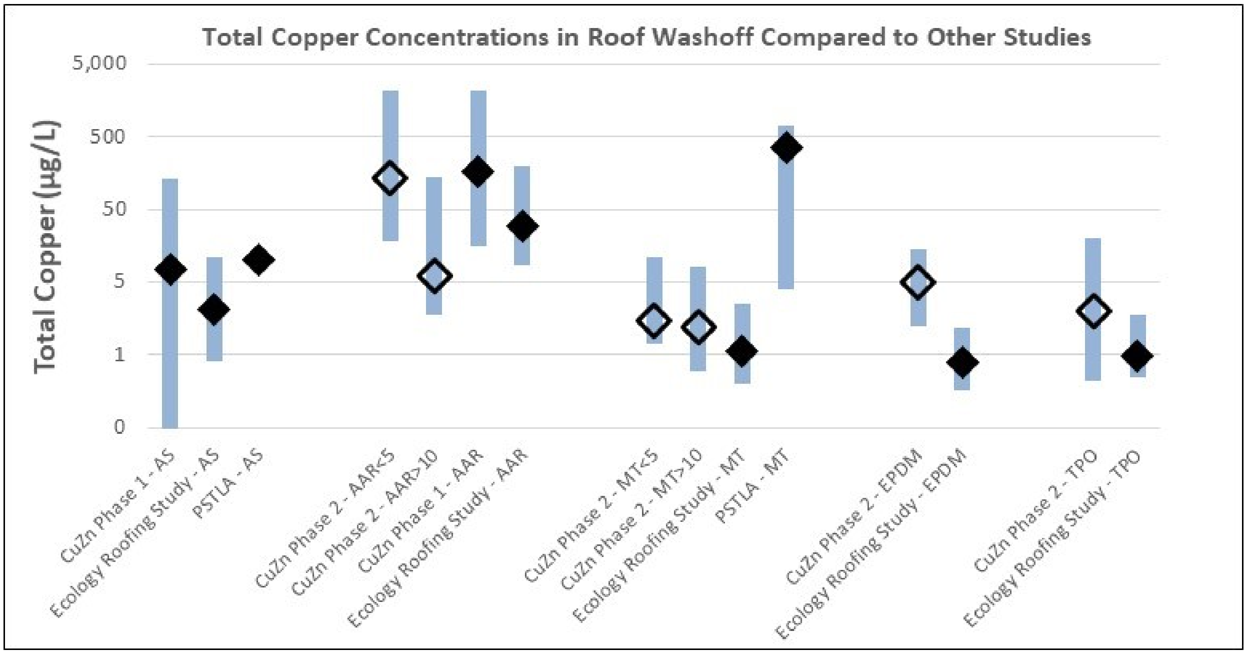

Figure 25. Total copper concentrations in roof washoff in *CuZn Phase 2* and those found in other studies. Bars represent minimum and maximum concentrations and diamonds represent medians, except for PSTLA results, where diamonds represent means. Open diamonds identify *CuZn Phase 2* medians. Note logarithmic scale on y-axis. AS = unfortified asphalt shingle; AAR = asphalt shingle with algae-resistant granules; MT = painted steel; EPDM = ethylene propylene diene terpolymer; TPO = thermoplastic polyolefin.

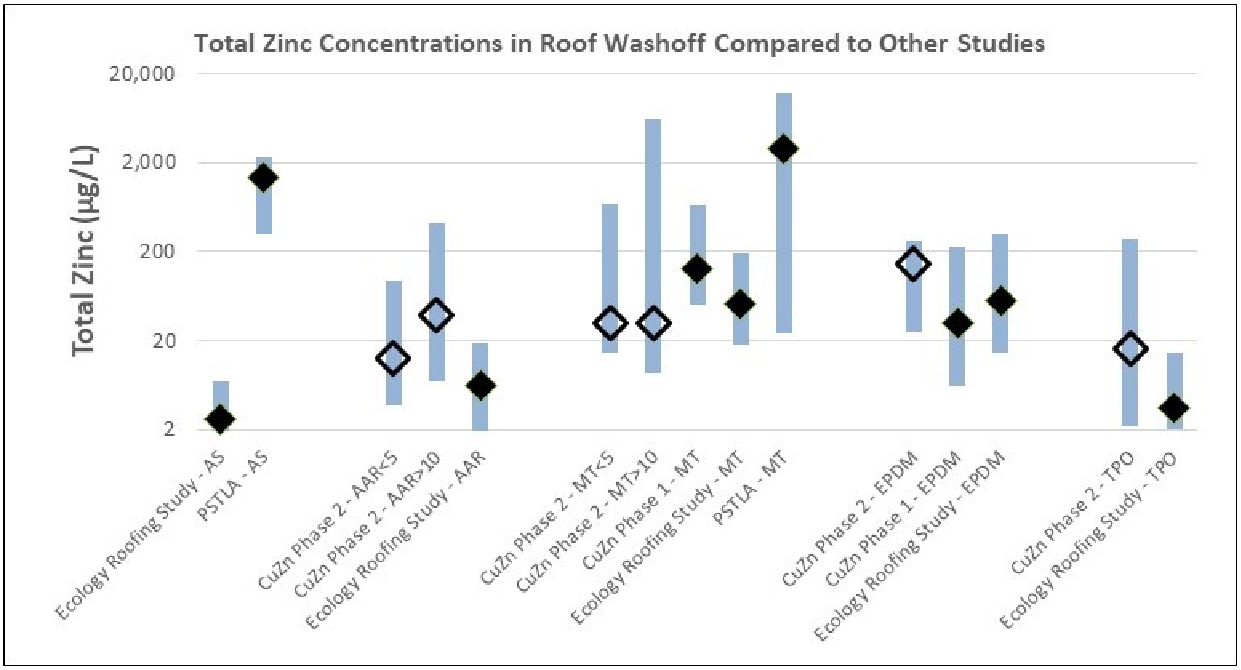

Figure 26. Total zinc concentrations in roof washoff in *CuZn Phase 2* and those found in other studies. Bars represent minimum and maximum concentrations and diamonds represent medians, except for PSTLA results, where diamonds represent means. Open diamonds identify *CuZn Phase 2* medians. Note logarithmic scale on y-axis. AS = unfortified asphalt shingle; AAR = asphalt shingle with algae-resistant granules; MT = painted steel; EPDM = ethylene propylene diene terpolymer; TPO = thermoplastic polyolefin.

Copper and Zinc Releases from Roofs and Gutters in the Study Area

Unit area release rates of copper and zinc were calculated for all roof and gutter materials sampled for *CuZn Phase 2*. The release rates are expressed as the mass of copper or zinc released per unit area in a given period. In order to compare release rates and loads to estimates derived in *CuZn Phase 1*, only total metals are considered.

Table 10 shows release rates for *CuZn Phase 2* and compares them with the same roof and gutter material types used for *CuZn Phase 1* estimates. For all roof types assessed, release rates calculated based on *CuZn Phase 2* results were lower than rates estimated during *CuZn Phase 1*. Release estimates from *CuZn Phase 1* were an order of magnitude higher for RAAR, RMT, and GUTT. The median release rate for *CuZn Phase 1* zinc in REPDM was about double that found during *CuZn Phase 2*. Some of the data used for the *CuZn Phase 1* release rate estimates were based on data corrected for atmospheric deposition (e.g., from the Roofing Study); had corrected rates not been used, the differences between *CuZn Phase 1* and *CuZn Phase 2* would be more pronounced.

The differences in unit area release rates between *CuZn Phase 1* and *CuZn Phase 2* generally reflect copper and zinc concentrations in roof washoff. The notable exception is zinc released from REPDM. Based on median zinc concentrations in washoff, one would expect higher zinc release rates from the *CuZn Phase 2* results. It is not clear what caused this discrepancy. One possibility is that the surface area contributing to washoff was overestimated, which would lead to lower unit area release rates.

For *CuZn Phase 2*, GUTT release rates were calculated as storm event releases from each metal roof subtracted from its companion roof/gutter combination. In a few cases, event releases of copper and zinc were higher in the roof than in the roof/gutter combination, leading to calculated rates that are negative.

Roof types sampled for *CuZn Phase 2* represent 48.2% of roof area in the study area, and gutter types represent 17.0% of gutter area. Table 11 shows total annual mass copper and zinc releases for the study area based on the unit area release rates and the areas of materials being analyzed (see Equation 5, *Methods* section). The coverage areas of each material in the study area were estimated for the *CuZn Phase 1* study and are used to calculate annual releases for both *CuZn Phase 1* and *CuZn Phase 2*. Therefore, differences in annual mass releases calculated in each study phase reflect differences in unit area release rates (i.e., those in Table 10).

The combined median annual release of copper from all roofing and gutter materials analyzed in *CuZn Phase 2* was an order of magnitude lower than the estimate from *CuZn Phase 1* (5.5 kg/yr versus 40 kg/yr). Both studies estimate that the bulk of annual copper release is from RAAR; for *CuZn Phase 1* RAAR was the only material with comparable release rates. In the *CuZn Phase 2* study, the combined median annual copper release from metal roofing (RMT), ethylene propylene diene terpolymer (REPDM), thermoplastic polyolefin (RTPO), and gutters (GUTT) was less than 1 kg/yr.

Table 10. Total copper and zinc release rates for roofing and gutter materials from *CuZn Phase 1* and *CuZn Phase 2*.

Material type	**CuZn study phase**	**Total copper release rate (mg/m^2/yr)**				**Total zinc release rate (mg/m^2/yr)**			
		Min	*Median*	*Mean*	*Max*	*Min*	*Median*	*Mean*	*Max*
RAAR<5	**2**	**4.0**	**120**	**260**	**1,100**	**2.3**	**7.4**	**18**	**99**
RAAR>10	**2**	**0.28**	**5.9**	**11**	**87**	**2.3**	**34**	**51**	**270**
RAAR[a]	**2**	**0.28**	**19**	**130**	**1,100**	**2.3**	**20**	**34**	**270**
RAAR	1	16	160	260	2,200	ne	ne	ne	ne
RMT<5	**2**	**0.015**	**1.6**	**1.7**	**3.7**	**0.92**	**30**	**107**	**509**
RMT>10	**2**	**0.058**	**0.72**	**1.6**	**8.3**	**6.6**	**34**	**310**	**1,400**
RMT[b]	**2**	**0.015**	**1.2**	**1.7**	**8.3**	**0.92**	**32**	**210**	**1,400**
RMT	1	ne	ne	ne	ne	100	270	540	1,400
REPDM	**2**	**0.27**	**4.0**	**4.7**	**15**	**4.5**	**140**	**130**	**280**
REPDM	1	ne	ne	ne	ne	74	380	580	2,700
RTPO	**2**	**0.050**	**1.0**	**2.4**	**7.9**	**0.67**	**11**	**18**	**79**
RTPO	1	ne	ne	ne	ne	ne	ne	ne	ne
GUTT	**2**	**-2.5**	**0.16**	**0.051**	**1.3**	**-32**	**22**	**16**	**38**
GUTT[c]	1	ne	ne	ne	ne	100	270	540	1,400

RAAR = asphalt shingle with algae-resistant granules; RMT = painted steel; REPDM = ethylene propylene diene terpolymer; RTPO = thermoplastic polyolefin; GUTT = painted or epoxy-coated steel.

[a] *Pooled RAAR<5 and RAAR>10 results.*

[b] *Pooled RMT<5 and RMT>10 results.*

[c] *Gutters and downspouts associated with steep-sloped metal roofs.*

CuZn Phase 2 results are in bold font for emphasis.

ne = not estimated.

The combined median annual release of zinc from all roofing and gutter materials analyzed from *CuZn Phase 2* is estimated to be 21 kg/yr. Estimates of annual zinc releases from *CuZn Phase 1* are available for a wider variety of building materials than estimates for copper. The combined median annual release of zinc from all roofing and gutter materials was estimated to be 77 kg/yr, about four times the *CuZn Phase 2* estimate.

Median annual zinc releases are similar for each of the roof materials assessed during *CuZn Phase 2* (3.2–7.1 kg/yr), but are much lower for gutters (0.2 kg/yr). The *CuZn Phase 1* report estimated that three-quarters of the zinc released from roofing materials was from metal roofs (60 kg/yr).

Table 11. Estimates of total copper and zinc releases from selected roofing and gutter materials in the study area.

Material type	CuZn study phase	Area (m^2)	Total copper release (kg/yr)				Total zinc release (kg/yr)			
			Min	*Median*	*Mean*	*Max*	*Min*	*Median*	*Mean*	*Max*
RAAR[a]	**2**	**252,177**	**0.071**	**4.8**	**33**	**280**	**0.6**	**5.0**	**8.6**	**68.1**
RAAR	1	252,177	4.0	40	66	555	ne	ne	ne	ne
RMT[b]	**2**	**221,241**	**0.0033**	**0.27**	**0.38**	**1.8**	**0.20**	**7.1**	**46**	**310**
RMT	1	221,241	ne	ne	ne	ne	22	60	120[d]	310
REPDM	**2**	**37,445**	**0.010**	**0.15**	**0.18**	**0.56**	**0.17**	**5.2**	**4.9**	**10**
REPDM	1	37,445	ne	ne	ne	ne	2.8	14	22	100
RTPO	**2**	**288,826**	**0.014**	**0.29**	**0.69**	**2.3**	**0.19**	**3.2**	**5.2**	**23**
RTPO	1	288,826	ne	ne	ne	ne	ne	ne	ne	ne
GUTT	**2**	**9,124**	**-0.023**	**0.0015**	**0.00047**	**0.012**	**-0.29**	**0.20**	**0.15**	**0.35**
GUTT[c]	1	9,124	ne	ne	ne	ne	0.91	2.5	4.9	13
Total CuZn Phase 2 =			**0.075**	**5.5**	**34**	**285**	**0.87**	**21**	**65**	**411**
Total CuZn Phase 1 =			4.0	40	66	560	26	77	146	423

RAAR = asphalt shingle with algae-resistant granules, RMT = painted steel, REPDM = ethylene propylene diene terpolymer, RTPO = thermoplastic polyolefin, GUTT = painted or epoxy-coated steel.

[a] *Pooled RAAR<5 and RAAR>10 results.*

[b] *Pooled RMT<5 and RMT>10 results.*

[c] *Gutters and downspouts associated with steep-sloped metal roofs.*

[d] *Incorrectly reported as 79 kg/yr (173 lb./yr) in the CuZn Phase 1 report.*

CuZn Phase 2 results are in bold font for emphasis.

ne = not estimated.

Copper and Zinc Releases from Siding Materials

Copper and zinc concentrations in siding washoff were generally higher than those from roof and gutter materials. However, overall releases of copper and zinc in siding washoff were small compared to the roof materials examined.

Siding is generally only exposed to rain during wind-driven storms, and even then, only the windward side(s) of buildings generate washoff. Roof overhangs shield siding from exposure, as do trees, nearby buildings, and other standing structures.

While efforts were made to collect siding washoff from the “weather” side of the buildings sampled for *CuZn Phase 2*, the targeted siding produced little washoff. Less than two-thirds of the samples across all storm events had sufficient volume for metals analysis (approx. 100 mL), and of those, only one-half had enough volume to analyze dissolved metals.

Analysis of the washoff volumes collected from siding locations indicate that, on average, only about 1% of the storm precipitation contacted the siding to produce washoff. This does not necessarily indicate that only 1% of the area was exposed. A more likely scenario is that only a portion of the lower siding column was typically exposed to rain, with an increasing amount of exposure occurring nearer ground level. It should be noted that the 1% exposure estimate is based on locations where washoff was generated; this estimate could be revised downward if locations without measurable washoff are considered.

As a result of small washoff volumes generated for siding during *CuZn Phase 2*, release rates and mass releases of copper and zinc from selected siding materials were estimated to be small (Tables 12 and 13). The sum of median releases from painted fiberboard, metal, and wood were estimated to be only 0.009 kg/yr and 0.18 kg/yr for total copper and total zinc, respectively, even though the surface area of these materials constitute 30% of the total siding found in the study area.

Table 12. Total copper and zinc release rates for siding materials.

Material type	**CuZn study phase**	**Total copper release rate (mg/m^2/yr)**				**Total zinc release rate (mg/m^2/yr)**			
		Min	*Median*	*Mean*	*Max*	*Min*	*Median*	*Mean*	*Max*
SFBR	**2**	**0.0095**	**0.016**	**0.028**	**0.084**	**0.011**	**4.2**	**5.6**	**16**
SFBR[a]	1	nd	6.6	15	54	6.9	310	540	1,600
SMT<5	**2**	**0.0028**	**0.017**	**0.047**	**0.30**	**0.19**	**0.53**	**1.2**	**7.0**
SMT>10	**2**	**0.013**	**0.037**	**0.060**	**0.21**	**0.061**	**0.53**	**7.8**	**34**
SMT[b]	**2**	**0.0028**	**0.024**	**0.054**	**0.30**	**0.061**	**0.53**	**4.4**	**34**
SMT[c]	1	nd	nd	0.3	0.9	5.0	23	130	480
SWD	**2**	**0.0082**	**0.026**	**0.021**	**0.031**	**0.092**	**0.42**	**0.56**	**1.2**
SWD	1	nd	6.6	15	54	6.9	310	540	1,600

SFBR = painted fiberboard; SMT = painted steel; SWD = painted wood.

[a] *Painted fiberboard was not reported in* CuZn Phase 1*; painted wood values are used here.*

[b] *Pooled MT<5 and MT>10 results.*

[c] *Includes unpainted metals.*

CuZn Phase 2 results are in bold font for emphasis.

nd = not present at detectable concentrations.

Siding releases of copper and zinc calculated from *CuZn Phase 2* results are two to three orders of magnitude lower than estimates from *CuZn Phase 1*. For the *CuZn Phase 1* study, it was assumed that all of the siding in the study area is exposed to full precipitation. Since actual exposure is at least two orders of magnitude lower (i.e., ≤1%) than actual exposure area in *CuZn Phase 1* calculations, most of the differences in mass release estimates can be attributed to these exposure assumptions. By comparing washoff concentrations instead of annual mass releases, the exposure factor can be removed, and these are much closer between *CuZn Phase* 1 and *CuZn Phase 2*. Median washoff concentrations for both total copper and total zinc are generally higher for *CuZn Phase 1*, but within a factor of two, except for total zinc in metal siding, which is higher by a factor of five in *CuZn Phase 1*.

In addition to examining exposure assumptions, another question centers on what is actually being sampled in siding washoff. All of the siding materials sampled were painted; therefore, it seems unlikely that copper and zinc from underlying materials—in this case fiberboard, metal, and wood—are migrating to the painted surface. Some of the copper and zinc in washoff could leach from paint or originate in particulate form from weathered paint. In a study of urban metals sources, Davis et al. (2001) found that painted material was found to deliver no more copper than unpainted wood, and concluded that paint from siding was not a major contributor to overall copper loads. However, they found much higher concentrations of zinc in painted wood versus unpainted wood.

Zinc oxide (ZnO) is a common ingredient added to exterior paints to provide mildew resistance, corrosion inhibition, tint and film strength, and protection from ultraviolet light (Diebold et al., 2003). Zinc can be released due to weathering or leaching, and in extreme cases, zinc-rich paints formulated for corrosion protection can release enough zinc to cause toxicity to aquatic organisms in stormwater (Kszos et al., 2004).

Table 13. Estimates of total copper and zinc releases from selected siding materials in the study area.

Material type	CuZn study phase	Area (m^2)	Total copper release (kg/yr)				Total zinc release (kg/yr)			
			Min	*Median*	*Mean*	*Max*	*Min*	*Median*	*Mean*	*Max*
SFBR	**2**	**4,490**	**4.2 x 10^{-5}**	**7.1 x 10^{-5}**	**1.3 x 10^{-4}**	**3.8 x 10^{-4}**	**5.1 x 10^{-5}**	**0.019**	**0.025**	**0.070**
SFBR	1	4,490	nd	0.030	0.069	0.24	0.031	1.4	2.4	7.3
SMT[a]	**2**	**119,344**	**3.3 x 10^{-4}**	**0.0029**	**0.0064**	**0.036**	**0.0073**	**0.063**	**0.52**	**4.0**
SMT	1	119,344	ne	ne	ne	ne	12	32	64	160
SWD	**2**	**225,194**	**0.0019**	**0.0058**	**0.0048**	**0.0069**	**0.021**	**0.094**	**0.13**	**0.26**
SWD	1	225,194	nd	1.5	3.5	12	1.6	69	122	365
Total CuZn Phase 2 =			**0.0019**	**0.0087**	**0.011**	**0.043**	**0.028**	**0.18**	**0.68**	**4.3**
Total CuZn Phase 1 =			--	1.5	3.6	12	14	102	188	532

SFBR = painted fiberboard, SMT = painted steel, SWD = painted wood.

[a] Pooled SMT<5 and SMT>10 results.

CuZn Phase 2 results are in bold font for emphasis.

nd = not present at detectable concentrations.

ne = not estimated.

Accumulation of dirt and dust on siding materials also adds a confounding factor in interpreting results from siding washoff. While aerially borne dust is not likely to accumulate on siding to the same degree as for rooftops, wind-borne or resuspended dust and dirt is visually evident on almost all siding material. Wood and fiberboard siding would be expected to trap more dirt and dust due to its rough texture, but smooth metal siding also accumulates particulate matter.

Analysis of siding washoff generated from artificial rainwater appears to have done little to isolate the source of metals in the present study. This sampling occurred in mid-August and is more representative of a first-flush event than the storm event sampling. As mentioned previously, this sampling consisted of two sequential rinses of the target siding, with samples collected after each rinse. Concentrations of both copper and zinc were nearly always higher in the first rinse, suggesting that much of the accumulated dirt and dust was removed in this initial rinse. For filtered (dissolved) metals samples, filters were visibly darkened more in the first rinse and in some cases became clogged with particles. However, it is not known what portion of the metals originated from weathered paint versus metals contained in exogenous dirt and dust. It is also unclear why site-by-site comparisons nearly always showed higher concentrations in storm-generated samples versus artificial washoff from siding.

Copper and Zinc Releases from Light Standards and Chain-Link Fencing

As discussed in the *Results* section, zinc measured in *CuZn Phase 2* washoff from exposed galvanized materials – chain-link fencing (CNLNK) and light standards (LGT) – had the highest concentrations among all materials sampled. CNLNK and LGT washoff also had the highest unit area release rates for zinc, and aside from 30-year-old metal roofing, was the only material with rates greater than 1 g/m^2/yr.

A median unit area release rate of 2,200 mg/m^2/yr of total zinc was used in *CuZn Phase 1* to estimate loads from all galvanized steel materials, including light standards and chain-link fencing (Table 14). Since respective median values for CNLNK and LGT for *CuZn Phase 2* were estimated at 930 and 510 mg/m^2/yr, releases scaled to the study area were lower than *CuZn Phase 1* (Table 15).

Median and mean annual releases of total zinc from *CuZn Phase 2* CNLNK and LGT are similar in degree to the combined release calculated from roofing materials, even though their combined surface area is less than 7% of the combined roof and gutter surface area. Zinc releases from other galvanized materials (guardrails, cell towers) mentioned in the *CuZn Phase 1* report might also be expected to contribute substantial releases, even though their combined surface areas are comparatively small. Copper releases from galvanized materials are inconsequential relative to roof releases.

The degree to which light standards and chain-link fencing accumulate aerially deposited particles is not known. However, the high concentrations of zinc in washoff and the high dissolved zinc concentrations as a percentage of total zinc suggest that leaching of zinc from the materials rather than particle washoff is the primary mechanism of release.

Table 14. Total copper and zinc release rates for chain-link fencing and light standards.

Material type	**CuZn study phase**	**Total copper release rate (mg/m^2/yr)**				**Total zinc release rate (mg/m^2/yr)**			
		Min	*Median*	*Mean*	*Max*	*Min*	*Median*	*Mean*	*Max*
CNLNK	**2**	**0.086**	**0.53**	**0.54**	**1.6**	**280**	**930**	**940**	**1,700**
CNLNK	1	ne	ne	ne	ne	730	2,200	2,000	2,700
LGT	**2**	**0.032**	**0.16**	**0.17**	**0.32**	**100**	**510**	**500**	**1,000**
LGT	1	ne	ne	ne	ne	730	2,200	2,000	2,700

CNLNK = unpainted chain-link fencing; LGT = galvanized unpainted light standards.
CuZn Phase 2 results are in bold font for emphasis.
ne = not estimated.

Table 15. Estimates of total copper and zinc releases from chain-link fencing and light standards in the study area.

Material type	CuZn study phase	Area (m^2)	Total copper release (kg/yr)				Total zinc release (kg/yr)			
			Min	*Median*	*Mean*	*Max*	*Min*	*Median*	*Mean*	*Max*
CNLNK	**2**	**52,385**	**0.0045**	**0.028**	**0.028**	**0.085**	**15**	**49**	**49**	**89**
CNLNK	1	52,385	ne	ne	ne	ne	38	120	100	140
LGT	**2**	**2,039**	**3.2×10^{-5}**	**1.6×10^{-4}**	**1.7×10^{-4}**	**3.2×10^{-4}**	**0.21**	**1.04**	**1.02**	**2.1**
LGT	1	2,039	ne	ne	ne	ne	1.5	4.6	4.1	5.6
Total CuZn Phase 2 =			**0.0045**	**0.028**	**0.028**	**0.085**	**15**	**50**	**50**	**91**
Total CuZn Phase 1 =			ne	ne	ne	ne	40	125	104	146

CNLNK = unpainted chain-link fencing; LGT = galvanized unpainted light standards.
CuZn Phase 2 results are in bold font for emphasis.
ne = not estimated.

Implications for Receiving Waters

The most direct method of evaluating an aquatic contaminant from a nonpoint source involves quantifying concentrations in a waterbody, identifying the path in which the contaminant was delivered to the waterbody, and isolating the primary source from which the contaminant was initially released. For copper and zinc, a large amount of data are available on concentrations in the aquatic environment. For instance, since January 2000 more than 9,000 entries have been made to Ecology's Environmental Information Management (EIM) database for copper in freshwaters within the Puget Sound basin. Zinc results total nearly 8,000.

Numerous (likely in the thousands) results also exist for copper and zinc in stormwater, many of which are contained in discharge monitoring reports for various permits administered under the National Pollutant Discharge Elimination System (NPDES), including Municipal Stormwater Phase I and Phase II permits (the latter requires monitoring only under certain circumstances). Collectively, data from EIM, discharge monitoring reports, and other sources might provide a picture of copper and zinc in waterbodies and their delivery pathways. This may be especially true for highly developed areas with dense concentrations of industrial, commercial, and residential development.

The reader should be aware that the study area for *CuZn Phase 2* was not selected based on any specific concerns regarding copper or zinc. In fact, few places in western Washington have been identified as having impaired surface waters based on the state's list of impaired water (i.e., Clean Water Act Section 303(d)). There are 15 waterbodies in western Washington and four in eastern Washington listed as impaired due to copper. For zinc, there are four impairments statewide, all in western Washington. None of the impairments for either copper or zinc are in the two Water Resource Inventory Areas (WRIAs, essentially large river basins) in which *CuZn Phase 2* sites are located.

Inclusion on the 303(d) list is not the sole determinant for concern about possible effects to aquatic organisms (Norton et al, 2011a). This is especially true for copper, which can exert effects on salmonids well below water quality criteria (Meyer and Deforest, 2018). However, the 303(d) list is an effective method to identify waterbodies with substantial contaminant sources, particularly from nonpoint releases.

Perhaps most importantly, *CuZn Phase 2* and studies that have identified potentially large copper and zinc releases based on literature values (e.g., *CuZn Phase 1* and PSTLA) do not necessarily find links between releases and copper or zinc enrichment of receiving waters. The present study did not consider the fate or transport of copper and zinc once it was washed off of the materials being examined. On-site observations suggested that little if any of the washoff was conveyed overland to surface waterbodies or conveyance systems (e.g., storm drains). With few exceptions, washoff from materials examined (roofs, siding, gutters, chain-link fencing, and light standards) went directly into soil at the dripline and presumably remained on site, at least in the short term. Copper and zinc in particulate form likely becomes bound to surface soils permanently. Dissolved copper and zinc from roof runoff has been shown to migrate to soil layers deeper than 1 meter (Mason et al., 1999), but overall retention in surface soils is typically high and dependent on a variety of soil characteristics (Bertling, 2005).

These circumstances are notably different from vehicle-related releases of copper and zinc identified in *CuZn Phase 1*. Brake wear was estimated to release almost 60% of the copper in the study area, and tire and brake wear combined were estimated to release 15% of zinc. These releases may have a larger impact on receiving waters because releases occur on impervious surfaces, enhancing their potential conveyance and delivery to waterbodies.

Paulson et al. (2012) used these concepts and release rates for various chemicals, including copper, to develop conceptual models for two urbanized stream basins (Mill and Thornton Creeks) in the Puget Sound basin. They estimated that nearly all of the copper released from roofs was attenuated before reaching either creek, primarily through sequestration in soils. In total, they estimated that only 3% of the copper released in the Mill Creek basin and 7% of the copper released in the Thornton Creek basin was ultimately discharged by the creeks. Since the releases include those directly to impervious surfaces (primarily from vehicle sources), they concluded that little of the copper released from roofs reach these creeks.

A study to assess the impacts to receiving waters in the study area (Woodland Creek and some of its tributaries) would ideally include monitoring stations on these waterbodies located downstream of the study area. Field measurements of all major copper and zinc releases, evaluation of their fate and transport following initial release, and development of conceptual models is beyond the scope of the present study.

Although not built into the design for the present study, sampling of Woodland Creek was conducted for an unrelated study (Collyard and Anderson, 2017) at a location just downstream of the study area (although it did not include the entire drainage for the study area). Monthly sampling of various chemicals, including copper and zinc, was conducted at this station during 2015. Sampling was not focused on storm sampling. Nevertheless, low concentrations of copper and zinc were found, with most samples at nondetectable concentrations for copper (<0.5 µg/L) and zinc (<5 µg/L). Maximum concentrations were 2.1 µg/L for total copper and 14 µg/L for total zinc. It is notable that copper concentrations in Woodland Creek are about an order of magnitude lower than those in Mill and Thornton Creeks (Paulson et al., 2012).

While these data might suggest that washoff from buildings and other materials have little effect on the major receiving water in the study area drainage, more sampling of Woodland Creek and its tributaries would be needed as confirmation. Unfortunately, no stormwater data are available to aid in the assessment of copper and zinc in conveyance systems (the City of Lacey is not required to monitor copper and zinc in stormwater under conditions of their Municipal Phase II permit). This paucity of data would severely limit the development of conceptual models for copper and zinc in the study area, if it were to be a goal of further study.

Summary and Conclusions

The present field study (*CuZn Phase 2*) provides a follow-up study to literature-derived estimates of copper (Cu) and zinc (Zn) releases from selected materials in a small urban sub-watershed in western Washington (*CuZn Phase 1*; Bookter, 2017a) and from the entire Puget Sound basin (PSTLA; Norton et al., 2011a). *CuZn Phase 2* also supplements roofing washoff data generated from Ecology's Roofing Study (Winters et al., 2014).

Washoff from the following material types in the built environment were sampled during five or six rain events in 2018:

Roofing

- asphalt shingle roofs with algae-resistant granules <5 or >10 years old
- painted metal (steel) roofs <5 or >10 years old
- ethylene propylene diene terpolymer (EPDM) roofs
- thermoplastic polyolefin (TPO) roofs

Siding

- painted fiberboard (fiber cement) siding
- painted wood siding
- painted metal (steel) siding <5 or >10 years old

Other

- painted metal (steel) gutters
- galvanized light standards
- galvanized uncoated chain-link fencing

Bulk (wet + dry) atmospheric deposition samples were also collected.

The overall magnitude of copper and zinc releases calculated during the present study appears to be small. Table 16 shows a summary of estimated annual copper and zinc releases of all materials of interest within the study area. At the median level, approximately 6 kg copper and 70 kg zinc are released annually in the study area. By comparison, median annual copper and zinc releases from the same materials calculated for the *CuZn Phase 1* report were about 40 and 300 kg/yr, respectively. For *CuZn Phase 2,* the bulk of copper is from roof washoff (mainly from algae-resistant asphalt shingles) and the bulk of zinc is from uncoated chain-link fencing.

The *CuZn Phase 1* effort considered other anthropogenic sources of copper and zinc in the study area. The bulk (60%, avg. of 210 kg/yr) of the total copper release is estimated to be from brake wear, with another 10% (avg. of 34 kg/yr) related to other vehicle uses. Roof materials in *CuZn Phase 1* were found to contribute about one-quarter of the total copper releases, and siding material about 3%.

For zinc, *CuZn Phase 1* estimated that approximately 40% (avg. of 1,100 kg/yr) of the total annual release in the study area is from the application of moss control products. An additional one-third of total zinc release is due to vehicle use or related materials and activities. Siding materials together with chain-link, roofing materials, and gutters make up another one-quarter of total zinc releases according to *CuZn Phase 1*.

Since releases of copper and zinc from vehicle use and moss control products were not addressed in the present study, it is unknown how well *CuZn Phase 1* estimates might match up with field results. If *CuZn Phase 1* estimates of vehicle-related and moss control copper and zinc releases are accurate, the materials analyzed for *CuZn Phase 2* constitute only minor contributions to overall releases. On the other hand, if field studies find that *CuZn Phase 1* overestimated vehicle and moss control releases, the overall release of copper and zinc in the study area might be fairly small.

From a water quality perspective, an important component of copper and zinc is the conveyance from the point of release to receiving waters. This was not addressed in the present study, nor was it addressed in *CuZn Phase 1*. Some of the primary sources addressed in *CuZn Phase 1* suggest copper and zinc releases to impervious surfaces, such as vehicle use, are more likely to become mobile and have a higher likelihood of being delivered to surface waters.

Table 16. Estimates of total copper and zinc releases from selected materials in the study area.

	Total copper release (kg/yr)				**Total zinc release (kg/yr)**			
Material type	*Min*	*Median*	*Mean*	*Max*	*Min*	*Median*	*Mean*	*Max*
RAAR[a]	0.071	4.8	33	280	0.6	5.0	8.6	68.1
RMT[b]	0.0033	0.27	0.38	1.8	0.20	7.1	46	310
REPDM	0.010	0.15	0.18	0.56	0.17	5.2	4.9	10
RTPO	0.014	0.29	0.69	2.3	0.19	3.2	5.2	23
GUTT	-0.023	0.0015	0.00047	0.012	-0.29	0.20	0.15	0.35
Total roofing and gutter	**0.075**	**5.5**	**34**	**280**	**0.87**	**21**	**65**	**410**
SFBR	4.2×10^{-5}	7.1×10^{-5}	1.3×10^{-4}	3.8×10^{-4}	5.1×10^{-5}	0.019	0.025	0.070
SMT[b]	3.3×10^{-4}	0.0029	0.0064	0.036	0.0073	0.063	0.52	4.0
SWD	0.0019	0.0058	0.0048	0.0069	0.021	0.094	0.13	0.26
Total Siding	**0.0019**	**0.0087**	**0.011**	**0.043**	**0.028**	**0.18**	**0.68**	**4.3**
CNLNK	0.0045	0.028	0.028	0.085	15	49	49	89
LGT	3.2×10^{-5}	1.6×10^{-4}	1.7×10^{-4}	3.2×10^{-4}	0.21	1.04	1.02	2.1
Total light and chain-link	**0.0045**	**0.028**	**0.028**	**0.085**	**15**	**50**	**50**	**91**
Total all materials	**0.082**	**5.6**	**34**	**285**	**16**	**71**	**120**	**520**

RAAR = asphalt shingle with algae-resistant granules; RMT = painted steel; REPDM = ethylene propylene diene terpolymer; RTPO = thermoplastic polyolefin; GUTT = painted or epoxy-coated steel; SFBR = painted fiberboard; SMT = painted steel; SWD = painted wood; CNLNK = unpainted chain-link fencing; LGT = galvanized unpainted light standards.

[a] *Pooled AAR<5 and AAR>10 results.*

[b] *Pooled MT<5 and MT>10 results.*

From this sampling effort, the following conclusions can be drawn:

1) Overall, rain washoff from most roofing materials in the built environment does not contain high concentrations of copper or zinc compared with literature-based estimates (e.g., PSTLA [Norton et al., 2011a] and *CuZn Phase 1* [Bookter, 2017a]). This is consistent with findings from the Ecology Roofing Study (Winters et al., 2014).
2) Some roof types do release appreciable quantities of copper and zinc per unit area.
    a. Copper from newer asphalt shingle roofs (<5 years old) that use algae-resistant granules release copper at rates up to two orders of magnitude higher than other roof types analyzed.
    b. Copper releases from algae-resistant asphalt roofs appear to diminish as the roof ages. This is supported by the finding that copper from older asphalt shingle roofs (>10 years old) that use algae-resistant granules release copper at rates an order of magnitude lower than newer material.
    c. Zinc can be released at high concentrations by older painted metal roofs (30 years old). However, this finding is based on a single roof at this age. Five newer painted metal roofs (≤12 years old) or their companion metal painted gutters did not release high concentrations of zinc.
3) Washoff from painted siding has higher concentrations of zinc than roof washoff; copper concentrations are generally low. While not investigated for the present study, it is possible that weathered paint is the main source of zinc from siding washoff.
4) Materials that are composed almost exclusively of galvanized steel—chain-link fencing and light standards in the case of the present study—release high quantities of zinc but little copper. However, it does not appear that there is substantial enrichment of zinc in roof washoff due to rainwater contact with ancillary roofing components, such as fasteners and flashing, that might also be composed of galvanized steel.
5) Older materials composed of exposed or painted metals generally release more zinc than newer materials.
6) Most of the copper (70% on average) and zinc (90% on average) in washoff from all materials is in the dissolved form.
7) Mass quantities of copper and zinc released annually from all materials analyzed in the study area are lower than those from literature-based estimates (e.g., PSTLA and *CuZn Phase 1* studies).
8) The PSTLA study overestimated mass zinc releases from roofing in the Puget Sound basin.
9) Results of the present study provide a better indicator of regional copper and zinc releases than those typically found in the published literature.

Recommendations

Prioritizing Releases of Copper and Zinc

Copper and zinc have the potential to adversely impact surface waters. Releases of copper and zinc from nonpoint sources may be pronounced in urban areas due to the abundance of materials and activities that can shed these metals into the environment. As a result, controlling conveyance sources (e.g., stormwater) is favored over cleanup, and in some cases, preventing their initial release might be a preferred option.

To set priorities to reduce initial release of copper or zinc from materials and activities, several questions should be considered:

- What materials or activities are likely to release the most copper and zinc?
- Are copper and zinc released in a form or location where they can become mobile?
- Are there known impacts to surface waters due to copper and zinc releases from specific materials or activities?

The weight given to each question might depend on the goals of source control efforts. For the present study, only the initial question was addressed (What materials or activities are likely to release the most copper and zinc?), and only selected source materials were investigated. As a result, context is limited and the importance of the selected materials as source control priorities is thus limited as well. Future studies need not address all elements of copper and zinc releases and full assessment of their fate and transport, but consideration of these points will yield more information for prioritizing source control.

Recommendations for Sampling Copper and Zinc in Building Materials and Structures

Collecting bulk washoff from building materials that release metals during precipitation events is beset with opportunities for sample contamination. Conducting a study at a large scale requires numerous installations to provide washoff diversions and large volume collectors (≥200 L in some cases) at multiple sites. These sampling systems require setup immediately in advance of an anticipated storm event, and preparing for an event can be logistically cumbersome. If sampling devices are not completely sealed from the environment (other than washoff), they need to be recalled if a storm does not materialize.

In order to avoid these potential problems, investigators may want to consider artificial rainwater sampling for some materials. This may be best achieved using a phased approach. The initial phase would involve side-by-side collection and analysis of both rainwater washoff and artificial washoff. Results would be compared and artificial rainwater washoff could be modified until it closely matched rainwater washoff. Investigators should strive to replicate the physical characteristics of rainwater as well as the chemical characteristics. This includes the angle of descent, as well as the force at the point of contact (droplet size and velocity).

Once there is a high degree of confidence that artificial rainwater sampling provides a suitable substitute for storm washoff, artificial washoff sampling would provide a number of benefits.

Sampling could be conducted at any time and would not necessitate pre-storm setup. Adequate washoff volume could easily be generated from vertical surfaces. Sample collection devices could be smaller and simpler, and could be more easily isolated from contamination.

To assess chemical contributions from atmospheric deposition, it is recommended that sampling devices be deployed at each location where materials are sampled. This would provide a more accurate picture of site-specific atmospheric deposition and would help assess any contributions from localized sources. When sampling for metals, collection devices should be constructed of plastic, glass, or other non-metallic material.

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Glossary, Acronyms, and Abbreviations

Glossary

Anthropogenic: Human-caused.

Atmospheric deposition: Atmospheric deposition is the result of airborne chemicals settling onto the land or air surface through precipitation or deposition of dry particulate matter.

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

CuZn study area: A portion of the lower Woodland Creek watershed, primarily within the City of Lacey and part of Thurston County, Washington.

Nonpoint source: Pollution that enters any waters of the state from any dispersed land-based or water-based activities, including but not limited to atmospheric deposition; surface water runoff from agricultural lands, urban areas, or forest lands; subsurface or underground sources; or discharges from boats or marine vessels not otherwise regulated under the NPDES program. Generally, any unconfined and diffuse source of contamination. Legally, any source of water pollution that does not meet the legal definition of "point source" in section 502(14) of the Clean Water Act.

Parameter: Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

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

Point source: Sources of pollution that discharge at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites where more than 5 acres of land have been cleared.

Rainwater runoff: Precipitation that falls on and flows over a surface.

Rinsate: Laboratory-supplied reagent-grade deionized water that has flowed over (i.e., rinsed) a container or sample equipment.

Salmonid: Fish that belong to the family *Salmonidae*. Species of salmon, trout, or char.

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.

Total suspended solids (TSS): Portion of solids retained by a filter.

Turbidity: Relative clarity of a liquid. Turbidity can be used as a surrogate indicator of TSS.

Washoff: Portion of precipitation or sprayed water that flows off of a constructed surface.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector, such as a stream, river, or lake at a lower elevation.

303(d) list: Section 303(d) of the federal Clean Water Act requires Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water — such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality–limited estuaries, lakes, and streams that fall short of state surface water quality standards and are not expected to improve within the next 2 years.

Acronyms and Abbreviations

AAR	Asphalt shingles with algae-resistant granules
AS	Asphalt shingles, a roofing material
CNLNK	Chain-link fencing
Cu	Copper
DOC	Dissolved organic carbon
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
EPDM	Ethylene propylene diene terpolymer
FBR	Fiberboard
GIS	Geographic information system
HVAC	Heating, ventilation, and air conditioning
ICP-MS	inductively coupled plasma mass spectrometry
LGT	Light standard
MEL	Manchester Environmental Laboratory
MPTFE	Modified polytetrafluoroethylene
MT	Metal roofing or siding material
NPDES	National Pollutant Discharge Elimination System
NTU	Nephelometric Turbidity Unit
QA	Quality assurance
QAPP	Quality assurance project plan
QC	Quality control
PSTLA	Puget Sound Toxics Loading Assessment (Norton et al. 2011a)
RAAR	Roofing, asphalt shingles with algae-resistant granules
REPDM	Roofing, ethylene propylene diene terpolymer
RMT	Roofing, metal
RPD	Relative percent difference
RTPO	Roofing, thermoplastic polyolefin
S.C.	Specific conductivity
SFBR	Siding, fiberboard
SMT	Siding, metal
SWD	Siding, wood
S.U.	Standard Units
TOC	Total organic carbon
TPO	Thermoplastic polyolefin
TSS	Total suspended solids (see Glossary)
WAC	Washington Administrative Code
WD	Wood
WRIA	Water Resource Inventory Area
Zn	Zinc

Units of Measurement

°C	degrees centigrade
°F	degrees Fahrenheit
cm	centimeter, 1/100 meter
ft	feet
g	gram, a unit of mass
kg	kilograms, a unit of mass equal to 1,000 grams
km^2	square kilometer, equal to one million square meters
L	liter
m	meter
m^2	square meter
mg	milligram, a unit of mass equal to 1/1,000 gram
mg/L	milligrams per liter (parts per million)
mL	milliliter, 1/1000 of a liter
mm	millimeter, 1/1000 of a meter
µg	microgram, a unit of mass equal to one millionth gram
µg/L	micrograms per liter (parts per billion)
µm	micron (micrometer), one millionth of a meter
µM	micromole, one millionth of a mole
µS/cm	microsiemens per centimeter, a unit of conductivity
yr(s)	year(s)

Appendices

Appendix A

Table A-1. Sampling locations. All sites are in Lacey, Washington, unless otherwise noted.

	Material Information				Location Information		
Location ID	**Source**	**Type**	**Age (yrs)**	**Area* (m^2)**	**Latitude**	**Longitude**	**Address**
MARQ-RAAR	Roofing	AAR	1	45.0	47.05574	-122.75723	8515 Litt Dr NE
Mill-RAAR	Roofing	AAR	3	46.31	47.06177	-122.88280	1511 Miller Ave NE; Olympia
LCC-RAAR	Roofing	AAR	4	25.75	47.03957	-122.79380	6729 Pacific Ave SE
NEIL-RAAR	Roofing	AAR	10	37.73	47.05526	-122.78624	1210 Neil St NE
CALL-RAAR	Roofing	AAR	13	183.92	47.06949	-122.77978	2400 Callison Rd NE
MARV-RAAR	Roofing	AAR	19	138.60	47.05598	-122.76355	130 Marvin Rd SE
NRB-RMT	Roofing	Metal	<1	6.32	47.03787	-122.89767	1111 Washington St SE; Olympia
NTA-RMT	Roofing	Metal	2	23.45	47.04982	-122.83319	250 Sleater Kinney Rd NE
MECO-RMT	Roofing	Metal	4	3.42	47.06924	-122.77188	2527 Marvin Rd NE
CAC-RMT	Roofing	Metal	12	131.02	47.07607	-122.75064	3020 Willamette Dr NE
UNNAMED-RMT	Roofing	Metal	12	13.68	—	—	Lacey
SAND-RMT	Roofing	Metal	30	34.46	47.06063	-122.79736	1415 Sandy Ln NE
NRB-REPDM	Roofing	EPDM	3	87.40	47.03716	-122.89671	1111 Washington St SE; Olympia
RITE-REPDM	Roofing	EPDM	18	77.47	47.05728	-122.76604	8230 Martin Way E
ECHQ-REPDM	Roofing	EPDM	24	371.57	47.04752	-122.80779	300 Desmond Dr SE
MECO-RTPO	Roofing	TPO	4	22.21	47.06920	-122.77181	2527 Marvin Rd NE
SBY-RTPO	Roofing	TPO	8	22.09	47.08516	-122.83544	3845 Sleater Kinney Rd NE; Olympia
OBRI-RTPO	Roofing	TPO	10	173.22	47.03472	-122.90517	504 15th Ave SE; Olympia
ADON-SFBR	Siding	Fiber Cement	1	3.20	47.08194	-122.75358	8850 Adonis Ct NE
EAGL-SFBR	Siding	Fiber Cement	4	3.58	47.07777	-122.78585	3061 Eagle Lp NE
CAMP-SFBR	Siding	Fiber Cement	5	4.05	47.08915	-122.75809	4089 Campus Willows Lp NE
CAC-SWD	Siding	Painted Wood	12	1.73	47.07583	-122.75041	3020 Willamette Dr NE
NEIL-SWD	Siding	Painted Wood	14	1.56	47.05518	-122.78636	1210 Neil St NE
MILL-SWD	Siding	Painted Wood	29	2.07	47.06178	-122.88303	1511 Miller Ave NE; Olympia
CIRQ-SMT	Siding	Metal	1	7.24	47.07196	-122.76820	8276 28th Ct NE
NTA-SMT	Siding	Metal	2	4.77	47.04961	-122.83316	250 Sleater Kinney Rd NE
MECO-SMT	Siding	Metal	4	2.41	47.06935	-122.77183	2527 Marvin Rd NE
ECHQ-SMT	Siding	Metal	12	2.08	47.04752	-122.81003	300 Desmond Dr SE
FRES-SMT	Siding	Metal	16	1.70	47.05974	-122.75368	8770 Tallon Ln NE
SAND-SMT	Siding	Metal	30	2.62	47.06053	-122.79743	1415 Sandy Ln NE
NRB-GUTT	Gutters	Metal	<1	12.56	47.03787	-122.89767	1111 Washington St SE; Olympia
MECO-GUTT	Gutters	Metal	4	27.03	47.06930	-122.77190	2527 Marvin Rd NE
UNNAMED-GUTT	Gutters	Metal	12	46.12	—	—	Lacey
PNR-LGT	Streetlight	Galvanized	8	13.47	47.04961	-122.81632	Martin Way Park-n-Ride
E109-LGT	Streetlight	Galvanized	>30	14.46	47.04931	-122.81673	Exit 109 northbound I-5 on-ramp
E111-LGT	Streetlight	Galvanized	>30	14.46	47.06296	-122.76324	Exit 111 northbound I-5 on-ramp
ECOC-CNLNK	Chain-link	Galvanized	7	0.43	47.07248	-122.76893	8270 28th Ct NE
PNR-CNLNK	Chain-link	Galvanized	8	0.35	47.04938	-122.81638	Martin Way Park-n-Ride

	Material Information				Location Information		
Location ID	**Source**	**Type**	**Age (yrs)**	**Area* (m^2)**	**Latitude**	**Longitude**	**Address**
SBY-CNLNK	Chain-link	Galvanized	>11	0.43	47.08522	-122.83550	3845 Sleater Kinney Rd NE
ECHQ-ATM	Atmospheric Deposition		-	0.18	47.04773	-122.80829	300 Desmond Dr SE
HUGH-ATM	Atmospheric Deposition		-	0.18	47.07212	-122.76750	8284 28th Ct NE

**Area of surface producing washoff samples.*
AAR = asphalt shingle with algae-resistant granules; Metal = painted steel;
EPDM = ethylene propylene diene terpolymer; TPO = thermoplastic polyolefin.

Appendix B

Table B-1. Sample containers, preservation, and holding times.

Parameter	Matrix	Minimum Quantity	Container	Preservative**	Holding Time
Total metals	water	350 mL*	500 mL poly	1:1 HNO_3 ≤6°C	6 months
Dissolved metals	water	350 mL*	500 mL poly Nalgene filter	Filter, 1:1 HNO_3 ≤6°C	6 months
Dissolved organic carbon	water	125 mL	125 mL n/m poly 0.45 µm filter	Filter, 1:1 HCl ≤6°C	28 days
Total suspended solids	water	1000 mL	1000 mL w/m poly	≤6°C	7 days
Hardness	water	100 mL	125 mL w/m poly	1:1 H_2SO_4 ≤6°C	6 months

** 500 mL required for low-level metals analysis.*

*** Samples will be collected within 24 hours of the end of a storm event. Sample filtering and preservation will be performed within 15 minutes of sample collection.*

n/m = narrow mouth; w/m = wide mouth.

Appendix C

Table C-1. Complete results of laboratory and field measurements. ***Bold italic*** font indicates an average of duplicates; * Calculated volume; NA = not analyzed.

Storm	Sample ID	Volume (L)	Total Cu (µg/L)	Dissolved Cu (µg/L)	Total Zn (µg/L)	Dissolved Zn (µg/L)	Hardness (mg/L)	DOC (mg/L)	TSS (mg/L)	pH	S.C. (µS)	Temp. (°C)	Turbidty (NTU)
1	MARQ-RAAR	288*	***62.7***	***40.4***	***3.9***	***2.9***	5.56	2.44	2	6.92	16.7	5.71	1.84
2	MARQ-RAAR	488*	65.5	48.0	12.9	4.6	8.70	3.01	4	7.09	26.9	13.7	2.0
3	MARQ-RAAR	200	1390	1300	21.8	15.5	20.5	82.4	67	5.81	69.8	14.4	14.9
4	MARQ-RAAR	123	602	563	9.5	8.7	24.0	46.3	13	6.22	59.9	22.1	5.25
5	MARQ-RAAR	949*	151	110	7.0	5.8	7.85	8.02	10	6.35	21.5	21.9	1.38
1	MILL-RAAR	371*	21.0	17.5	22.5	21.0	7.03	2.91	1	7.54	15.6	4.12	1.05
2	MILL-RAAR	105	17.9	16.7	25.7	25.9	7.55	3.43	1	7.15	17.6	7.26	0.68
3	MILL-RAAR	318*	299	234	93.7	82.6	17.3	79.6	27	5.32	75.8	11.1	14.1
4	MILL-RAAR	153	125	110	44.1	39.0	26.6	44.9	16	6.28	6.3	15.0	2.53
5	MILL-RAAR	976*	53.0	44.9	24.4	22.8	12.7	14.4	5	6.46	30.3	14.5	1.77
1	LCC-RAAR	139	134	118	4.3	6.5	2.03	1.12	1	6.61	6.4	4.62	1.20
2	LCC-RAAR	119	132	110	6.4	5.5	2.40	1.28	2	6.67	8.8	5.89	1.16
3	LCC-RAAR	85.7	2170	1950	15.5	15.9	12.5	43.7	24	5.98	41.8	11.6	9.80
4	LCC-RAAR	22.9	815	574	12.3	8.1	8.64	20.1	19	6.42	84.8	14.2	12.3
5	LCC-RAAR	163	495	410	7.1	7.3	7.33	10.2	5	6.38	20.0	15.6	1.40
1	NEIL-RAAR	302*	2.02	1.68	7.1	6.7	10.9	4.45	2	7.10	25.1	4.14	0.97
2	NEIL-RAAR	409*	1.76	1.75	7.5	7.5	11.7	5.11	1	6.95	28.9	6.95	0.70
3	NEIL-RAAR	156	136	18.8	418	111	23.0	197	53	4.85	167	10.8	1240
4	NEIL-RAAR	54.4	20.2	16.0	67.1	65.7	31.4	107	16	6.02	99.9	14.4	5.10
5	NEIL-RAAR	124	12.5	8.93	43.5	38.8	21.9	90.9	22	5.95	93.0	14.2	5.04
1	CALL-RAAR	152	2.56	1.86	21.2	17.4	13.2	3.90	4	6.99	32.3	4.59	1.50
2	CALL-RAAR	1993*	2.30	1.29	31.9	24.3	13.5	2.53	7	7.41	31.3	4.90	1.50
3	CALL-RAAR	1261*	15.0	12.6	83.7	61.3	15.6	73.9	39	6.33	68.3	10.8	11.3
4	CALL-RAAR	677	5.62	4.97	24.8	24.4	12.3	15.8	5	6.47	27.3	12.9	1.50
5	CALL-RAAR	3877*	6.21	3.85	40.3	21.9	10.7	10.2	55	7.05	22.8	12.9	3.81
1	MARV-RAAR	1109*	2.55	2.21	28.3	28.4	12.5	3.32	1	6.96	33.4	4.40	0.94
2	MARV-RAAR	1502*	2.82	2.61	36.6	37.5	18.0	3.30	1	7.31	44.4	7.61	0.75
3	MARV-RAAR	951*	15.2	14.4	93.9	86.6	15.3	38.0	9	6.30	67.1	11.8	3.0
4	MARV-RAAR	199	20.1	18.3	95.5	89.9	23.1	38.3	5	6.46	60.2	15.4	1.60
5	MARV-RAAR	2922*	7.57	6.28	38.5	34.2	9.78	8.09	5	6.81	23.1	15.6	0.80
1	NRB-RMT	68.7	***1.55***	***0.64***	***20.7***	***15.5***	0.54	0.68	3	5.90	5.4	4.27	1.70
2	NRB-RMT	82.3	0.97	0.58	17.1	18.3	0.57	1.02	3	6.18	6.9	8.88	1.0
3	NRB-RMT	39.7	3.44	2.95	32.7	29.1	3.04	10.9	32	5.61	22.1	12.9	15.0

Storm	Sample ID	Volume (L)	Total Cu (µg/L)	Dissolved Cu (µg/L)	Total Zn (µg/L)	Dissolved Zn (µg/L)	Hardness (mg/L)	DOC (mg/L)	TSS (mg/L)	pH	S.C. (µS)	Temp. (°C)	Turbidty (NTU)
4	NRB-RMT	18.7	3.42	2.52	42.5	33.3	3.08	22.2	23	5.67	18.7	16.9	4.55
5	NRB-RMT	125	1.69	1.35	15.0	12.2	1.57	4.24	4	5.29	9.5	17.9	1.30
1	NTA-RMT	188*	0.98	0.70	348	334	1.51	1.03	2	6.51	7.0	4.63	1.20
2	NTA-RMT	254*	0.70	0.60	373	382	1.48	0.85	2	6.47	7.9	6.73	0.80
3	NTA-RMT	0.2	11.2	NA	696	NA	NA	NA	NA	NA	NA	NA	NA
4	NTA-RMT	86.4	***3.53***	***2.63***	***482***	***458***	4.86	10.0	17	5.76	17.6	16.2	3.40
5	NTA-RMT	67.9	1.93	1.34	340	313	4.17	4.02	22	6.15	9.2	16.2	0.93
1	MECO-RMT	41.6	1.87	0.37	31.2	12.7	0.82	0.50	7	6.13	5.8	6.93	2.50
2	MECO-RMT	36.1	1.21	0.40	22.8	13.2	0.63	0.87	5	6.94	5.8	12.7	1.50
3	MECO-RMT	29.7	1.33	1.31	16.9	16.6	1.75	4.93	7	6.21	12.8	15.2	5.30
4	MECO-RMT	14.4	1.29	0.88	20.5	18.1	1.52	3.50	9	5.97	0.2	18.1	2.60
5	MECO-RMT	77.7	0.73	0.53	15.7	14.9	0.99	1.92	10	5.80	6.1	15.8	1.10
1	CAC-RMT	1048*	0.61	0.28	18.2	15.7	0.62	0.59	3	6.05	3.7	4.94	1.80
2	CAC-RMT	1420*	0.60	0.68	30.1	30.8	1.33	0.82	2	6.28	11.0	8.75	0.88
3	CAC-RMT	899*	7.87	3.32	97.2	53.2	6.65	28.9	154	5.93	45.3	11.3	38
4	CAC-RMT	483	1.80	0.97	32.3	24.9	2.30	5.02	11	5.82	10.0	13.1	3.40
5	CAC-RMT	2762*	1.89	1.08	25.5	21.2	1.58	3.33	5	6.11	9.1	15.3	1.06
1	UNNAMED-RMT	81.8	0.29	0.20	9.1	10.5	1.0	0.74	1	6.21	3.9	4.17	0.90
2	UNNAMED - RMT	124	0.28	0.23	8.5	8.5	0.58	0.93	1	6.28	4.9	5.75	0.66
3	UNNAMED - RMT	94*	3.51	1.00	45.0	13.1	2.60	15.8	170	6.00	8.8	10.5	50
4	UNNAMED - RMT	47.8	1.20	0.75	10.2	11.4	1.44	9.35	5	5.80	10.9	13.1	1.75
5	UNNAMED - RMT	189	1.05	0.46	9.5	8.9	1.11	5.06	5	6.43	9.0	13.7	1.64
1	SAND-RMT	276*	0.37	0.16	1090	1210	1.07	0.50	2	6.50	6.9	3.99	3.30
2	SAND-RMT	373*	0.41	0.32	1310	1340	1.30	0.77	1	6.85	9.6	5.63	1.08
3	SAND-RMT	4.2	3.07	1.83	6240	6360	24.0	125	28	6.21	2.4	9.70	7.50
4	SAND-RMT	35.7	6.53	0.72	2220	1160	9.11	16.2	141	6.4	30.0	11.6	40
5	SAND-RMT	726	***1.44***	***0.74***	***911***	***806***	1.38	4.20	23	6.14	12.4	15.7	2.04
1	NRB-REPDM	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2	NRB-REPDM	37.5	6.58	0.51	107	55.8	2.68	1.36	139	5.93	26.3	9.63	18.0
3	NRB-REPDM	599*	7.07	6.29	32.9	132	3.57	30.9	45	5.90	37.6	16.6	9.30
4	NRB-REPDM	322*	3.87	2.25	164	131	3.39	24.4	53	5.31	21.0	22.3	10.0
5	NRB-REPDM	1843*	1.32	1.18	120	120	2.09	8.55	5	5.30	13.1	34.0	1.30
1	RITE-REPDM	620*	9.55	0.35	25.6	11.5	0.36	3.96	1	6.84	9.3	12.0	1.28
2	RITE-REPDM	183	2.25	0.47	45.0	23.1	0.94	1.64	17	6.72	15.5	23.0	0.60
3	RITE-REPDM	204	10.0	8.77	130	89.9	2.82	44.4	50	6.26	55.6	20.7	9.90

Storm	Sample ID	Volume (L)	Total Cu (µg/L)	Dissolved Cu (µg/L)	Total Zn (µg/L)	Dissolved Zn (µg/L)	Hardness (mg/L)	DOC (mg/L)	TSS (mg/L)	pH	S.C. (µS)	Temp. (°C)	Turbidty (NTU)
4	RITE-REPDM	208	4.98	4.31	204	197	3.68	33.9	10	5.56	25.8	3.05	1.78
5	RITE-REPDM	1633*	3.54	2.71	268	250	2.24	16.4	54	5.32	17.9	34.5	3.60
1	ECHQ-REPDM	2973*	1.68	1.46	177	169	8.61	1.75	1	7.64	24.6	9.51	0.88
2	ECHQ-REPDM	4078	***1.25***	***1.36***	***116***	***119***	7.54	1.54	1	6.90	21.6	7.11	0.60
3	ECHQ-REPDM	2548*	14.4	13.2	234	189	9.76	82.6	19	6.20	75.5	9.60	5.40
4	ECHQ-REPDM	1368*	6.86	5.97	255	237	10.5	69.5	13	5.93	46.1	9.76	2.85
5	ECHQ-REPDM	7833*	4.76	4.28	186	185	11.7	17.2	64	6.29	30.1	15.0	2.0
1	MECO-RTPO	141*	5.71	1.98	53.3	3.9	1.25	45.7	39	NA	NA	NA	NA
2	MECO-RTPO	0.55	20.5	1.14	277	42.3	NA	NA	NA	NA	NA	NA	NA
3	MECO-RTPO	129	2.73	3.06	11.9	17.0	8.15	17.5	4	6.76	21.2	18.4	4.0
4	MECO-RTPO	33.5	4.08	3.46	15.7	12.8	9.06	20.2	32	6.65	21.2	26.9	2.90
5	MECO-RTPO	151	1.99	1.47	16.0	16.7	3.88	6.05	149	6.93	10.7	19.6	1.0
1	SBY-RTPO	208	0.22	0.09	2.2	2.2	0.75	0.50	1	6.35	2.8	3.65	1.30
2	SBY-RTPO	239*	***0.34***	***0.19***	***3.2***	***2.9***	0.66	0.78	2	6.06	4.6	5.01	1.12
3	SBY-RTPO	152*	1.34	0.93	16.4	13.1	3.22	7.08	20	5.92	15.1	11.1	7.0
4	SBY-RTPO	81.4	0.50	0.44	16.0	13.6	3.42	5.41	2	6.12	11.7	15.2	1.72
5	SBY-RTPO	466*	0.35	0.20	5.8	4.7	2.19	1.93	5	6.19	7.2	16	1.12
1	OBRI-RTPO	1386*	0.93	0.41	18.7	17.1	0.59	0.53	12	7.30	3.7	8.90	0.65
2	OBRI-RTPO	1071	0.57	0.42	15.9	16.3	0.84	0.77	1	6.97	7.5	7.49	0.60
3	OBRI-RTPO	1102	***7.15***	***7.55***	***81.0***	***30.0***	5.29	25.0	17	NA	NA	NA	NA
4	OBRI-RTPO	423	11.3	10.1	30.0	25.2	6.17	21.4	45	6.13	31.2	17.3	2.55
5	OBRI-RTPO	3652	***5.91***	***4.07***	***21.2***	***11.4***	3.57	6.51	34	6.41	11.5	28.5	1.50
1	ADON-SFBR	1.0	0.26	0.10	191	185	0.84	0.81	NA	NA	NA	NA	NA
2	ADON-SFBR	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2.5	ADON-SFBR	3.35	***0.52***	***0.39***	***295***	***277***	1.75	2.08	4	7.62	15.9	9.41	5.00
3	ADON-SFBR	0.38	4.64	0.98	688	610	NA	NA	NA	NA	NA	NA	NA
4	ADON-SFBR	0.2	1.75	NA	873	NA	NA	NA	NA	NA	NA	NA	NA
5	ADON-SFBR	0.4	2.36	1.62	1760	1730	NA	NA	NA	NA	NA	NA	NA
1	EAGL-SFBR	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2	EAGL-SFBR	0.1	3.47	NA	4.2	NA	NA	NA	NA	NA	NA	NA	NA
2.5	EAGL-SFBR	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
3	EAGL-SFBR	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
4	EAGL-SFBR	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
5	EAGL-SFBR	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
1	CAMP-SFBR	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2	CAMP-SFBR	0.4	1.62	NA	11.2	NA	NA	NA	NA	NA	NA	NA	NA

Storm	Sample ID	Volume (L)	Total Cu (µg/L)	Dissolved Cu (µg/L)	Total Zn (µg/L)	Dissolved Zn (µg/L)	Hardness (mg/L)	DOC (mg/L)	TSS (mg/L)	pH	S.C. (µS)	Temp. (°C)	Turbidty (NTU)
2.5	CAMP-SFBR	0.35	17.1	3.81	40.2	26.9	NA	NA	NA	NA	NA	NA	NA
3	CAMP-SFBR	0.04	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
4	CAMP-SFBR	0.02	90.0	NA	79.4	NA	NA	NA	NA	NA	NA	NA	NA
5	CAMP-SFBR	0.4	6.48	4.39	184	143	NA	NA	NA	NA	NA	NA	NA
1	CAC-SWD	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2	CAC-SWD	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2.5	CAC-SWD	0.03	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
3	CAC-SWD	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
4	CAC-SWD	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
5	CAC-SWD	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
1	NEIL-SWD	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2	NEIL-SWD	0.02	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2.5	NEIL-SWD	0.1	5.04	NA	56.1	NA	NA	NA	NA	NA	NA	NA	NA
3	NEIL-SWD	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
4	NEIL-SWD	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
5	NEIL-SWD	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
1	MILL-SWD	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2	MILL-SWD	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2.5	MILL-SWD	0.2	20.8	NA	338	NA	NA	NA	NA	NA	NA	NA	NA
3	MILL-SWD	0.05	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
4	MILL-SWD	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
5	MILL-SWD	0.4	7.21	5.98	274	249	NA	NA	NA	NA	NA	NA	NA
1	CIRQ-SMT	0.2	0.93	NA	109	NA	NA	NA	NA	NA	NA	NA	NA
2	CIRQ-SMT	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2.5	CIRQ-SMT	2.3	0.69	0.69	46.5	50.7	1.43	1.90	8	NA	NA	NA	NA
3	CIRQ-SMT	0.4	2.13	1.76	67.2	43.9	NA	NA	NA	NA	NA	NA	NA
4	CIRQ-SMT	0.2	2.84	NA	82.4	NA	NA	NA	NA	NA	NA	NA	NA
5	CIRQ-SMT	3.7	0.94	0.77	49.6	46.6	1.09	2.14	6	6.50	9.6	21.6	3.40
1	NTA-SMT	0.4	1.58	NA	107	NA	NA	NA	NA	NA	NA	NA	NA
2	NTA-SMT	0.1	6.50	NA	210	NA	NA	NA	NA	NA	NA	NA	NA
2.5	NTA-SMT	2.15	4.27	0.82	176	107	2.40	2.77	123	NA	NA	NA	NA
3	NTA-SMT	0.2	4.76	NA	118	NA	NA	NA	NA	NA	NA	NA	NA
4	NTA-SMT	0.03	26.7	NA	446	NA	NA	NA	NA	NA	NA	NA	NA
5	NTA-SMT	0.9	6.62	2.70	228	120	4.81	NA	NA	NA	NA	NA	NA
1	MECO-SMT	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2	MECO-SMT	0.15	12.2	NA	285	NA	NA	NA	NA	NA	NA	NA	NA
2.5	MECO-SMT	0.55	40.6	39.2	594	541	NA	NA	NA	NA	NA	NA	NA
3	MECO-SMT	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

Storm	Sample ID	Volume (L)	Total Cu (µg/L)	Dissolved Cu (µg/L)	Total Zn (µg/L)	Dissolved Zn (µg/L)	Hardness (mg/L)	DOC (mg/L)	TSS (mg/L)	pH	S.C. (µS)	Temp. (°C)	Turbidty (NTU)
4	MECO-SMT	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
5	MECO-SMT	0.7	44.1	31.6	1040	864	28.4	NA	NA	NA	NA	NA	NA
1	ECHQ-SMT	0.35	0.85	NA	11.7	NA	NA	NA	NA	NA	NA	NA	NA
2	ECHQ-SMT	0.1	3.63	NA	21.7	NA	NA	NA	NA	NA	NA	NA	NA
2.5	ECHQ-SMT	2.6	2.33	0.94	19.3	10.1	2.35	4.50	25	NA	NA	NA	NA
3	ECHQ-SMT	0.15	11.9	NA	95.4	NA	NA	NA	NA	NA	NA	NA	NA
4	ECHQ-SMT	0.03	11.3	NA	79.0	NA	NA	NA	NA	NA	NA	NA	NA
5	ECHQ-SMT	0.2	7.15	NA	34.0	NA	NA	NA	NA	NA	NA	NA	NA
1	FRES-SMT	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2	FRES-SMT	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2.5	FRES-SMT	0.1	17.1	NA	99.2	NA	NA	NA	NA	NA	NA	NA	NA
3	FRES-SMT	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
4	FRES-SMT	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
5	FRES-SMT	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
1	SAND-SMT	1.43	0.89	0.50	160	152	0.74	1.16	8	NA	NA	NA	NA
2	SAND-SMT	0.85	1.69	0.91	325	326	1.78	2.82	NA	NA	NA	NA	NA
2.5	SAND-SMT	4.25	0.88	0.88	261	259	0.80	1.79	3	NA	NA	NA	NA
3	SAND-SMT	0.63	5.82	4.32	744	599	4.89	NA	NA	NA	NA	NA	NA
4	SAND-SMT	0.2	9.73	NA	2040	NA	NA	NA	NA	NA	NA	NA	NA
5	SAND-SMT	1.4	4.93	3.61	441	413	4.51	18.2	NA	7.05	23.6	14.4	3.25
1	NRB-GUTT	156	1.21	0.90	39.5	37.8	0.80	1.17	1	6.60	6.2	4.93	0.98
2	NRB-GUTT	184	1.14	0.95	39.2	38.3	0.89	1.84	1	5.88	6.2	9.80	0.62
3	NRB-GUTT	71.6	3.93	3.08	79.5	60.7	2.90	6.95	6	5.92	15.1	13.7	6.0
4	NRB-GUTT	45.3	***4.04***	***3.58***	***70.0***	***68.1***	2.37	10.6	2	6.09	16.8	18.4	1.02
5	NRB-GUTT	265*	1.51	1.29	46.2	44.7	1.69	5.72	3	5.76	19.8	21.1	1.30
1	MECO-GUTT	182	0.65	0.34	21.1	21.0	0.52	0.50	1	5.87	5.3	5.32	1.05
2	MECO-GUTT	293*	0.64	0.44	22.9	22.5	0.51	0.58	1	6.18	4.7	11.6	0.56
3	MECO-GUTT	155	1.81	1.64	26.8	27.0	1.47	5.02	2	5.79	12.0	15.3	3.90
4	MECO-GUTT	88.6	2.02	1.63	28.4	26.5	1.30	3.92	2	5.92	8.4	16.7	0.92
5	MECO-GUTT	570*	0.94	0.73	20.0	20.7	0.73	1.36	2	5.65	5.4	16.3	0.70
1	UNNAMED - GUTT	370*	0.38	0.24	13.5	13.5	0.96	0.89	1	6.11	4.7	3.84	0.82
2	UNNAMED - GUTT	500*	0.41	0.28	19.4	17.2	0.99	0.92	1	6.09	6.3	5.75	0.54
3	UNNAMED - GUTT	316*	3.38	2.11	66.1	53.6	2.63	48.8	56	5.37	48.7	10.4	15.7
4	UNNAMED - GUTT	170	1.73	1.13	30.9	26.7	1.92	15.5	14	5.67	18.3	13.4	3.95
5	UNNAMED - GUTT	972*	1.79	0.54	26.9	17.2	1.78	4.80	17	6.09	7.8	13.3	4.10
1	PNR-LGT	3.0	2.30	1.54	8780	8420	0.76	4.41	NA	NA	NA	NA	NA

Storm	Sample ID	Volume (L)	Total Cu (µg/L)	Dissolved Cu (µg/L)	Total Zn (µg/L)	Dissolved Zn (µg/L)	Hardness (mg/L)	DOC (mg/L)	TSS (mg/L)	pH	S.C. (µS)	Temp. (°C)	Turbidty (NTU)
2	PNR-LGT	2.9	1.52	1.07	7680	7800	0.53	1.95	4	NA	NA	NA	NA
3	PNR-LGT	1.95	4.14	3.13	9700	8350	2.32	8.22	34	NA	NA	NA	NA
4	PNR-LGT	0.9	4.48	3.92	12200	12500	1.91	8.86	NA	NA	NA	NA	NA
5	PNR-LGT	2.8	4.19	3.75	9660	9470	1.46	7.34	2	7.10	48.2	19.4	1.05
1	E109-LGT	6.7	3.75	1.33	11800	11100	1.27	1.93	9	6.85	39.7	3.66	2.30
2	E109-LGT	9.0	3.93	2.04	10300	9910	1.10	2.0	10	7.00	46.2	6.48	2.80
3	E109-LGT	3.5	***8.45***	***4.12***	***16500***	***15100***	2.68	10.5	35	6.93	71.0	10.9	9.80
4	E109-LGT	1.4	7.20	5.12	21600	22900	3.58	13.8	43	NA	NA	NA	NA
5	E109-LGT	7.4	4.96	3.61	14700	14900	1.59	6.01	7	6.65	58.4	13.9	0.63
1	E111-LGT	11.6	2.74	1.61	8880	8820	0.83	2.18	5	6.72	32.5	6.06	1.77
2	E111-LGT	17.2	1.42	0.80	8940	8950	0.67	1.76	3	6.91	39.6	11.5	1.15
3	E111-LGT	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
4	E111-LGT	1.5	9.14	5.59	22500	22100	2.07	13.1	18	NA	NA	NA	NA
5	E111-LGT	10.3	4.21	2.05	12000	12100	0.92	3.23	7	6.55	46.2	20.4	1.80
1	ECOC-CNLNK	0.5	0.55	0.38	7250	7310	NA	NA	NA	NA	NA	NA	NA
2	ECOC-CNLNK	1.05	2.20	1.17	3880	3790	2.42	6.16	NA	NA	NA	NA	NA
3	ECOC-CNLNK	0.2	3.40	NA	7400	NA	NA	NA	NA	NA	NA	NA	NA
4	ECOC-CNLNK	0.1	24.9	NA	21800	NA	NA	NA	NA	NA	NA	NA	NA
5	ECOC-CNLNK	0.4	15.1	10.8	14300	14100	NA	NA	NA	NA	NA	NA	NA
1	PNR-CNLNK	0.15	12.8	NA	13300	NA	NA	NA	NA	NA	NA	NA	NA
2	PNR-CNLNK	0.1	14.4	NA	9890	NA	NA	NA	NA	NA	NA	NA	NA
3	PNR-CNLNK	0.05	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
4	PNR-CNLNK	<0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
5	PNR-CNLNK	1.0	11.2	6.92	4020	3470	129	1580	NA	7.44	5451	19.2	25.6
1	SBY-CNLNK	0.75	2.33	0.79	7310	6900	2.38	NA	NA	NA	NA	NA	NA
2	SBY-CNLNK	0.7	1.21	0.72	7700	7500	0.91	NA	NA	NA	NA	NA	NA
3	SBY-CNLNK	0.63	2.66	2.09	6630	7550	4.77	NA	NA	NA	NA	NA	NA
4	SBY-CNLNK	0.1	4.11	NA	17300	NA	NA	NA	NA	NA	NA	NA	NA
5	SBY-CNLNK	0.6	2.90	2.31	13900	13800	1.70	NA	NA	NA	NA	NA	NA
1	ECHQ-ATM	1.5	275	260	44.9	44.2	0.30	0.50	5	NA	NA	NA	NA
2	ECHQ-ATM	2.05	35.7	23.0	15.2	9.0	0.46	0.73	7	7.51	3.5	5.98	1.83
3	ECHQ-ATM	1.35	23.1	11.5	19.8	8.6	2.24	11.1	158	NA	NA	NA	NA
4	ECHQ-ATM	0.78	8.53	3.41	14.8	9.5	1.36	NA	NA	NA	NA	NA	NA
5	ECHQ-ATM	0.5	52.6	8.36	112	38.3	NA	NA	NA	NA	NA	NA	NA
5	ECHQ-ATM	3.23	2.91	2.17	6.9	6.1	0.51	0.79	3	6.32	9.2	12.8	1.70
1	HUGH-ATM	1.25	225	196	18.9	10.6	0.46	0.50	NA	NA	NA	NA	NA
2	HUGH-ATM	1.75	17.2	11.7	7.0	5.1	0.42	0.87	9	NA	NA	NA	NA
3	HUGH-ATM	1.25	16.1	7.69	13.2	7.2	1.70	5.32	49	NA	NA	NA	NA

Storm	Sample ID	Volume (L)	Total Cu (µg/L)	Dissolved Cu (µg/L)	Total Zn (µg/L)	Dissolved Zn (µg/L)	Hardness (mg/L)	DOC (mg/L)	TSS (mg/L)	pH	S.C. (µS)	Temp. (°C)	Turbidty (NTU)
4	HUGH-ATM	0.8	19.8	12.9	23.6	24.2	NA	NA	NA	NA	NA	NA	NA
5	HUGH-ATM	0.4	12.2	7.04	32.4	8.6	NA	NA	NA	NA	NA	NA	NA
5	HUGH-ATM	4.20	1.34	1.02	4.3	4.7	0.55	0.87	2	5.65	9.3	11.2	0.85