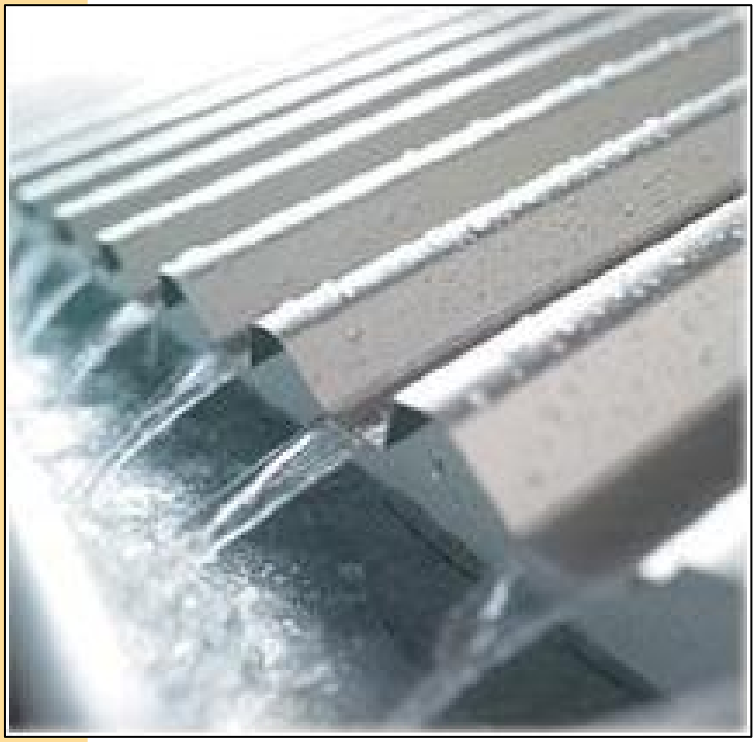

Quality Assurance Project Plan

Copper and Zinc in Urban Runoff: Phase 2 – Rainwater Runoff Monitoring

December 2017
Publication No. 17-03-117

DEPARTMENT OF
ECOLOGY
State of Washington

Publication Information

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

This Quality Assurance Project Plan is available on Ecology's website at https://fortress.wa.gov/ecy/publications/SummaryPages/1703117.html

Data for this project will be available on Ecology's Environmental Information Management (EIM) website: www.ecy.wa.gov/eim/index.htm. Search on Study ID ABOO0001.

Ecology's Activity Tracker Code for this study is 16-066.

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Quality Assurance Project Plan

Copper and Zinc in Urban Runoff:
Phase 2 – Rainwater Runoff Monitoring

December 2017

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EAP: Environmental Assessment Program
NEP: National Estuary Program
WQP: Water Quality Program

1.0 Table of Contents

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2.0 Abstract

Copper and zinc are two of the top five pollutants of concern entering the Puget Sound. The *Puget Sound Toxics Loading Assessment* found that the highest concentrations of copper and zinc are in surface runoff from areas of commercial and industrial land use. Quantities of copper and zinc are of concern in Puget Sound, because of their potential to harm aquatic organisms.

The *Copper and Zinc in Urban Runoff* study will evaluate the relative contributions of known sources of copper and zinc in a commercial and industrial area. This information will be useful in prioritizing source control actions. The study has been divided into two phases. Phase 1 estimated potential loading from various sources in the northeast portion of Lacey, Washington. Phase 2 will monitor copper and zinc concentrations in rainwater runoff from primary sources in the same study area.

The sources of copper and zinc selected for Phase 2 monitoring are building roofing and siding, chain-link fencing, streetlights, and roof gutters. These sources had the highest potential to contribute copper or zinc to the environment and the greatest variability around the Phase 1 estimated loading values. The Phase 2 results will be used to reduce the uncertainty of the Phase 1 loading estimates, fill data gaps, and to develop local release rates for the monitored sources of copper and zinc.

This quality assurance project plan (QAPP) describes the study's Phase 2 monitoring effort. Rainwater from construction materials and atmospheric deposition will be collected. The samples will be analyzed for total and dissolved metals (copper, zinc), dissolved organic carbon, total suspended sediment, water hardness, pH, conductivity, and turbidity.

3.0 Background

3.1 Introduction and problem statement

The *Puget Sound Toxics Loading Assessment* (PSTLA) identified copper (Cu) and zinc (Zn) as two of the top five pollutants of concern due to their potential to harm the health of Puget Sound. Because of the quantity released to Puget Sound, there is potential to harm aquatic organisms (Norton et al., 2011). Progress has been made in understanding the sources, fate, and transport of Cu and Zn in urban runoff. However, data gaps and uncertainty still exist that limit our ability to develop a comprehensive source control strategy.

Stormwater runoff from roadways and construction materials have been shown to be toxic to aquatic organisms. Runoff from industrial roofs are toxic to rainbow trout, flathead minnows, and aquatic invertebrates (Bailey et al., 1999; Tobiason and Logan, 2000). Urban stormwater is contributing to pre-spawning mortality of Coho salmon in streams on the west coast of the United States (Spromberg et al., 2016). Copper in stormwater runoff increases juvenile salmon susceptibility to predation (McIntyre et al., 2012).

The presence of free metal ions (Cu^{2+}, Zn^{2+}) is related to the bioavailability and toxicity of Cu and Zn in stormwater runoff (Heijerick et al., 2002; USEPA, 1985). The presence of free metal ions is influenced by the pH and hardness of water (USEPA, 1980; USEPA, 1985). In addition, the bioavailability of metal ions declines in the presence of dissolved organic carbon and suspended particles. Dissolved metal ions are highly reactive and can form strong complexes and precipitates with dissolved organic carbon and suspended particulates (Bertling, 2005; Joshi and Balasubramanian, 2010).

Many studies have assessed the sources of Cu and Zn in urban runoff. The PSTLA found that surface runoff is the major delivery pathway for both Cu and Zn to Puget Sound. The highest Cu and Zn concentrations are measured in stormwater runoff from commercial and industrial areas (Norton et al., 2011; Hobbs et al., 2015).

The Washington State Department of Ecology's (Ecology's) 2013-2014 roofing assessment study evaluated the contribution of pollutants from individual roofing materials. This was accomplished by constructing experimental roofing panels that isolated specific roofing materials from other roofing components. Ecology recommended that other roofing components (e.g., flashings, gutters, downspouts, fasteners, HVAC systems) and exposed galvanized materials (e.g., fencing, guardrails, and light posts) be evaluated as sources of metals in storm runoff (Winters et al., 2014).

In response to the recommendations of the above studies, the primary sources of Cu and Zn in a commercial and industrial area bordering Puget Sound were analyzed (Bookter, 2017). The sources in the built environment with the highest potential to contribute Cu or Zn to the environment and the greatest uncertainty around the estimated loading values are recommended for further investigation. Suggested sources for monitoring in the built environment include: parking lots, building roofing and siding materials, streetlights, and roof gutters.

3.2 Study area and surroundings

The *Copper and Zinc in Urban Runoff* (CuZn) study area is a 7.2 square-mile portion of the lower Woodland Creek watershed in the City of Lacey and part of Thurston County (Figure 1). Woodland Creek is in the Henderson Inlet watershed.

The 2016 land use in the study area is 35.5% commercial/industrial, 13.6% residential, 33.9% undeveloped, 12.4% roadways, 2.9% parks, and 1.8% agricultural. Of the area currently developed, 66% is commercial/industrial land use (Figure 2). The study area is undergoing rapid development (Collyard and Anderson, 2017).

The 2010 land use for the 12 counties bordering the Puget Sound is approximately 18.5% commercial/industrial, 47.5% residential, 32.4% undeveloped, and 1.6% agricultural. The land use profile of the CuZn study area compares more closely with land use in concentrated urban areas.

Bookter (2017) used U.S. census data to estimate the 2010 population of the CuZn study area at approximately 7,600. The approximate 2010 population of the 12 Puget Sound counties is 4.47 million.

The climate of the CuZn study area is temperate. The average annual precipitation between 2003 and 2016 was 39.5 inches (1003 mm). The annual number of days of rain varied from 104 to 169 in that same period (Thurston, 2017). The average annual temperature was 49.7˚F (9.8˚C) and varies from an average low of 39˚F to an average high of 60˚F (CLRSearch, 2017).

3.2.1 History of study area

The CuZn study area is located approximately halfway between Seattle, Washington and Portland, Oregon. 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 McCord is located approximately 15 miles (24 km) north of the CuZn study area. This has resulted in increased development of large square-footage warehouses, apartment complexes, tract housing, and commercial services (e.g., big-box stores, strip malls, restaurants, banks).

3.2.2 Summary of previous studies and existing data

The potential release of Cu and Zn to the Puget Sound was evaluated in the *Puget Sound Toxic Loading Assessment*. The PSTLA found that Cu and Zn are delivered in the highest quantities in stormwater runoff from commercial and industrial areas (Norton et al., 2011). However, the PSTLA effort spanned all 12 Puget Sound counties and could not evaluate the importance of individual sources of Cu and Zn.

Winters et al. (2014) performed a follow-up study to the PSTLA investigating the release of chemicals of concern from roofing materials. The roofing assessment collected rainwater runoff from experimental roofing panels and analyzed the concentrations of metals and other pollutants. They found that Cu is released from copper, asphalt shingle, and wood shake roofing materials. In addition, Zn is released from painted metal, polyvinyl chloride, ethylene propylene terpolymer, and wood shake roofing materials. Winters et al. (2014) recommend that other roofing components (e.g., flashings, gutters, downspouts, fasteners, HVAC systems) and exposed galvanized materials (e.g., fencing, guardrails, and light posts) be evaluated as sources of metals in storm runoff.

The current study is a continuation of the above research. Phase 1 of the *Copper and Zinc in Urban Runoff* (CuZn) study evaluated the potential release of Cu and Zn from known sources in the urban environment using literature release rates and GIS analysis. Phase 1 compiled urban Cu and Zn source data from research performed around the world. Bookter (2017) estimates that 800 pounds of Cu and 5,900 pounds of Zn are released each year in the CuZn study area. The primary sources of Cu are vehicle brake wear, roofing materials, parking lots, treated lumber, building siding, and vehicle exhaust. The main sources of Zn are moss control products, building siding, parking lots, vehicle tire wear, chain-link fence, roofing materials, and vehicle brake wear.

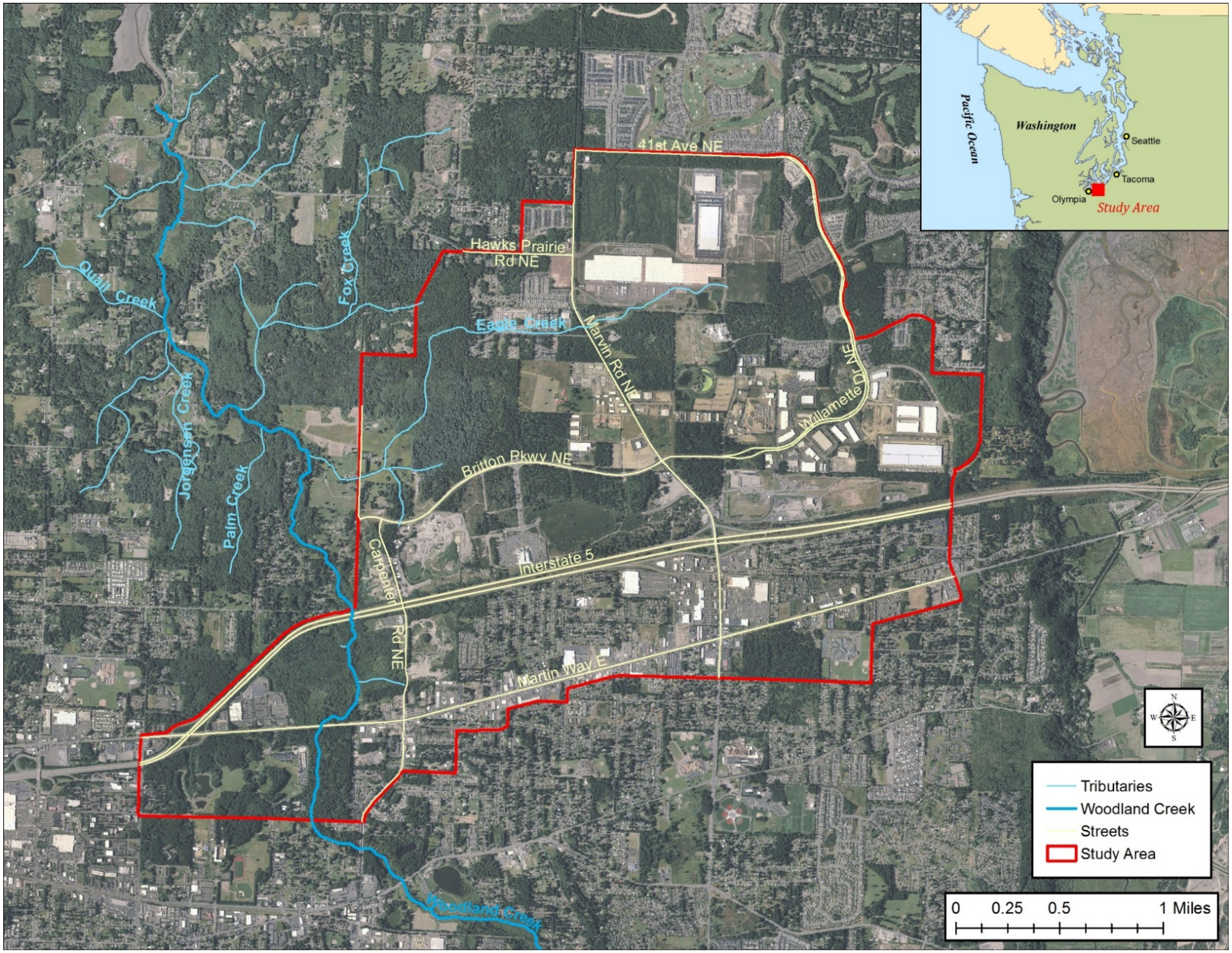

Figure 1. Map of the urban copper and zinc study area.

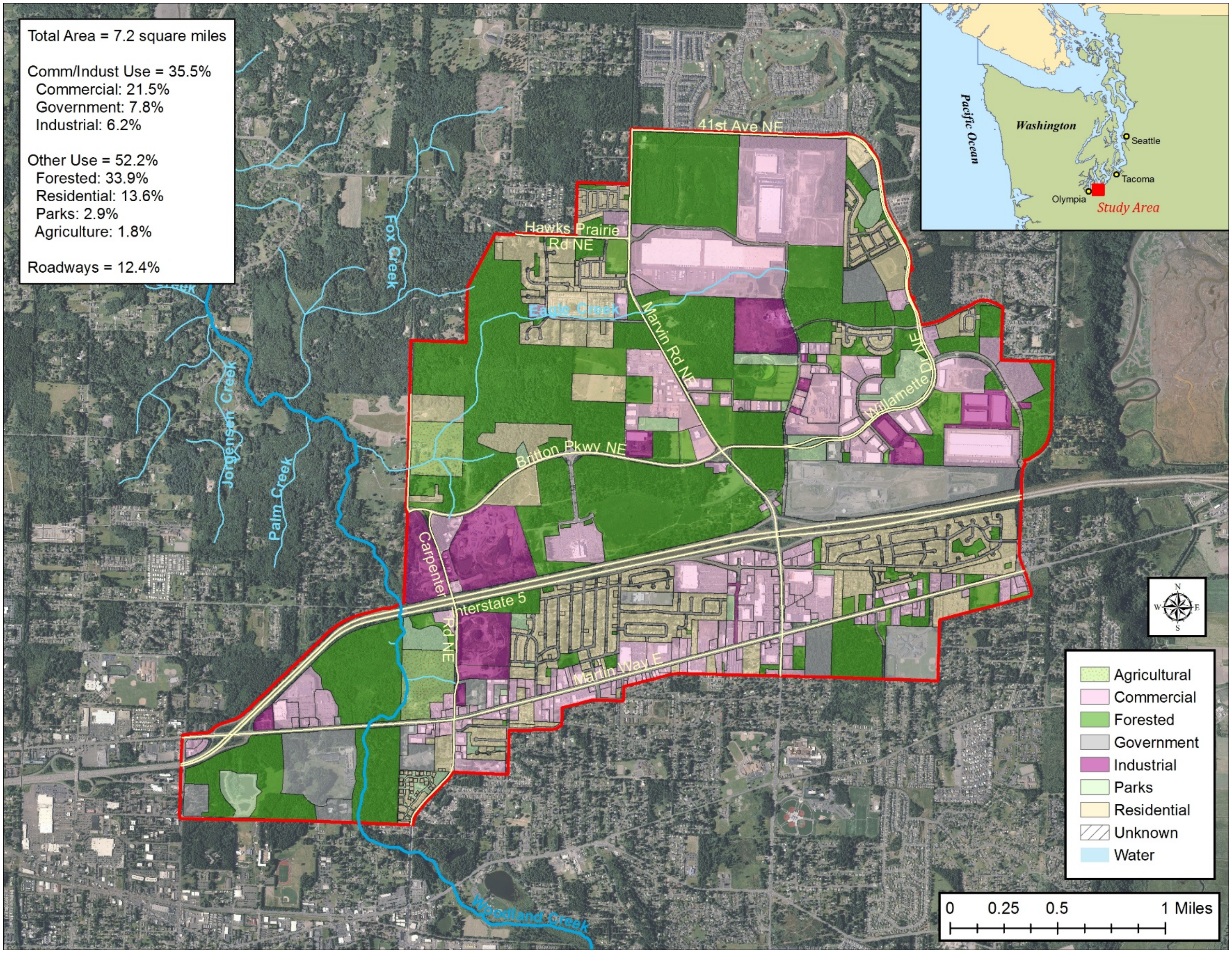

Figure 2. Map of land use in the urban copper and zinc study area, 2016.

The goal of the CuZn study is to identify potential sources of Cu and Zn in the urban environment and attempt to fill in data gaps in the current knowledge regarding those sources. Phase 1 identified sources and data gaps. The sources in the built environment with the highest potential to contribute Cu or Zn to the environment and the greatest variability around the estimated loading values are recommended for monitoring during Phase 2 of the CuZn study. These sources are parking lots, building roofing and siding materials, streetlights, and roof gutters (Bookter, 2017).

This quality assurance project plan (QAPP) details the monitoring plan for Phase 2 of the CuZn study.

3.2.3 Parameters of interest and potential sources

The monitoring detailed in this QAPP is designed to evaluate the quantity and bioavailability of Cu and Zn contributed by various construction materials. To accomplish this, rainwater samples from the materials will be analyzed for total and dissolved metals (Cu, Zn), dissolved organic carbon (DOC), water hardness, total suspended solids (TSS), pH, conductivity, and turbidity. Rainwater samples will be collected from building roofing and siding materials, chain-link fence, streetlight poles, and roof gutters.

Atmospheric deposition samples will be collected to account for the quantity of Cu and Zn deposited on construction materials from the air. Metals present in the atmosphere may be the result of industrial emissions or resuspension of road dust, including vehicle wear particles. Bulk atmospheric deposition (i.e., both wet and dry deposition) samples will be analyzed for total and dissolved metals (Cu, Zn). If sufficient sample volume is collected, then atmospheric deposition samples will also be analyzed for DOC, water hardness, pH, conductivity, and turbidity (in that order of priority).

Synthetic leaching samples may be collected instead of rainwater samples. To produce leaching samples, a known volume of synthetic rainwater, with a pH similar to natural rainwater, will be applied to the material surfaces. The leachate will be analyzed for total and dissolved metals (Cu, Zn), DOC, water hardness, TSS, pH, conductivity, and turbidity. Leaching samples will be collected for the following reasons.

- Not enough storm events with adequate rainfall volume are sampled.
- Insufficient rainwater runoff from building siding materials can be collected.

Further detail about the sample types listed above are provided in Section 8.2.

3.2.4 Regulatory criteria or standards

No regulatory criteria or standards apply to the rainwater collected in this study.

The monitoring for this study will sample rainwater runoff directly from construction materials, before that runoff is treated by any stormwater best management practices (BMPs). BMPs are designed to remove the majority of metals from stormwater before it reaches the receiving waters (Clary et al., 2011).

Stormwater benchmarks will be used for comparative purposes only. The industrial stormwater general permit (ISGP) benchmarks are a tool for assessing the effectiveness of facility BMPs. These benchmarks are applied to facility effluent where it is discharged to receiving waters. In this study, the rainwater runoff from construction materials will be collected upstream of facility discharge points.

Table 1. Washington State ISGP stormwater benchmarks.

Parameter	Matrix	Benchmark Concentration
Turbidity	Stormwater	25 NTU
pH	Stormwater	5.0 – 9.0
Oil Sheen	Stormwater	None Visible
Total Copper	Stormwater	Western WA: 14 ug/L
		Eastern WA: 32 ug/L
Total Zinc	Stormwater	117 ug/L

ISGP = industrial stormwater general permit (Ecology, 2015)
dw = dry weight

4.0 Project Description

The goal of the CuZn study is to build on existing data to develop a comprehensive data set of the relative importance of individual sources of Cu and Zn within an urban watershed. The focus of this study is on the *primary* release of Cu and Zn. Flows that transport Cu or Zn to the environment (e.g., stormwater runoff, air deposition, discharges from human activities) are not true sources, but conveyance of metals from the primary sources.

The results from this study will inform future source control efforts in the identification and reduction of important sources of Cu and Zn in commercial and industrial areas. Source control prioritization should incorporate the fate and transport of pollutants.

The scope of this study does not include the fate and transport of Cu and Zn released from primary sources. The loading values that will be reported are a representation of the release of Cu and Zn from construction materials, not the total loading of Cu and Zn in the receiving waters.

Phase 1 of the study identified sources of Cu and Zn in the urban environment. Potential Cu and Zn loading from urban sources were estimated using literature release rates and GIS analysis (Bookter, 2017).

This QAPP details Phase 2 of the CuZn study. Phase 2 will monitor the primary sources found in Phase 1 to have the highest potential to contribute Cu or Zn to the environment and the greatest variability around the estimated release values. This approach is anticipated to help refine release estimates for known sources Cu and Zn.

4.1 Project goals

The goal of Phase 2 of the CuZn study is to measure the quantity of Cu and Zn released from various materials and structures in the urban built environment.

4.2 Project objectives

To accomplish the project goals, the following objectives will be completed:

- Measure the quantity of Cu and Zn leached from materials in the urban environment
- Develop release rates for Cu and Zn from various construction materials
- Recalculate study area loading values using new release rates
- Compare release rates to Phase 1 data

4.3 Information needed and sources

Existing information needed for the study has been collected and incorporated into this QAPP. Further detail regarding potential sources of Cu and Zn in the urban built environment can be found in Bookter (2017).

Phase 2 of the CuZn study will result in new data for certain primary sources of Cu and Zn associated with commercial and industrial land use.

4.4 Tasks required

- Identify monitoring sites
- Analyze collection container Teflon liners for total recoverable metals (Cu, Zn)
- Prepare monitoring sites for sample collection
- Collect 234 rainwater runoff samples from construction materials
- Collect 12 bulk atmospheric deposition samples
- Analyze rainwater runoff samples for total and dissolved metals (Cu, Zn), DOC, TSS, water hardness, pH, conductivity, and turbidity
- Analyze bulk atmospheric deposition samples for total and dissolved metals (Cu, Zn)
  - If sample volume permits, analyze atmospheric deposition for DOC, water hardness, pH, conductivity, and turbidity
- Evaluate the preliminary Cu and Zn results
  - If the quantity of Cu and Zn present in the samples is less than the normal metals detection limits, then decrease the number of storm events monitored to match the available laboratory budget and the cost of the lower metals detection limit analysis
- Measure the contributing surface area for each sample collected
- Note other potential sources of Cu or Zn at each sample collection site
- Calculate release rates using Cu/Zn concentrations and contributing surface areas
- Perform Phase 1 source analyses using new release rates

4.5 Systematic planning process used

This Quality Assurance Project Plan (QAPP) represents the systematic planning process.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 2. Organization of project staff and responsibilities.

Staff (All EAP except client)	Title	Responsibilities
Diane Dent WQP-WM Phone: 360-407-6616	EAP Client	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP. Tracks progress on project deliverables.
Andy Bookter TSU-SCS Phone: 360-407-6530	Project Manager and Principal Investigator	Writes the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data. Analyzes and interprets data. Writes the draft report and final report.
Melissa McCall TSU-SCS Phone: 360-407-7384	Field and EIM Assistant	Helps collect samples and records field information. Enters data into EIM.
James Medlen TSU-SCS Phone: 360-407-6194	Field Assistant	Helps collect samples and records field information.
Debby Sargeant TSU-SCS Phone: 360-407-6771	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Jessica Archer SCS Phone: 360-407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Dale Norton WOS Phone: 360-407-6596	Section Manager for the Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Alan Rue Manchester Environmental Laboratory Phone: 360-871-8844	Acting Laboratory Director	Reviews and approves the final QAPP.
Tom Gries SCS Phone: 360-407-6327	NEP Quality Coordinator	Reviews draft QAPP and recommends approval of final QAPP. Reviews draft report and comments on consistency with final QAPP.
William R. Kammin Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP.

EAP: Environmental Assessment Program
EIM: Environmental Information Management database
NEP: National Estuary Program
QAPP: Quality Assurance Project Plan
SCS: Statewide Coordination Section
TSU: Toxic Studies Unit
WM: Watershed Management
WOS: Western Operations Section
WQP: Water Quality Program

5.2 Special training and certifications

Ecology staff responsible for field sampling are qualified to conduct work under this program through education and field experience. Relevant EAP standard operating procedures for water monitoring will be used. All staff will be experienced following these SOPs.

Monitoring sites in this study may require roof access. Ecology staff involved in sample collection on roofs with a fall hazard will be trained in proper fall protection protocols (Ecology, 2017).

5.3 Organization chart

See Table 2.

5.4 Proposed project schedule

Table 3. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	**Due date**	**Lead staff**
Field work started	December 2017	Andy Bookter
Field work completed	March 2018	Andy Bookter
Laboratory analyses completed	June 2018	
Environmental Information System database		
EIM Study ID	ABOO0001	
Product	**Due date**	**Lead staff**
EIM data loaded	July 2018	Melissa McCall
EIM data entry review	August 2018	Andy Bookter
EIM complete	September 2018	Melissa McCall
Final report		
Author lead / Support staff	Andy Bookter / James Medlen & Melissa McCall	
Schedule		
Draft due to supervisor	August 2018	
Draft due to client/peer reviewer	September 2018	
Draft due to external reviewer(s)	October 2018	
Final (all reviews done) due to publications coordinator	November 2018	
Final report due on web	December 2018	

5.5 Budget and funding

The total project budget for Phase 2 of the CuZn study is $307,603. This includes personnel time, equipment, and laboratory costs for six sample events.

The field and laboratory budget for the project is detailed in Table 4.

The number of sampling events monitored, and hence samples collected, is dependent on the observed metals concentrations in the runoff samples and the project budget. Metals analysis costs shown in Table 4 are for the lower cost, higher detection limit method (EPA200.8).

Initially, metals samples will be extracted and analyzed by ICP-MS following the protocols outlined in EPA method 200.8. If the Cu and Zn concentrations from the first storm event are below the method detection limit, then the remaining storm event metals analyses will be performed using the more sensitive, lower detection limit method (EPA1640/EPA200.8). This may require additional laboratory budget and will likely result in fewer sample events collected.

Table 4. Project budget detail of field and laboratory costs.

Water	**Samples**	**QA**	**Cost**	**Subtotal**
total metals (Cu, Zn)	234	50	$ 70	$ 19,880
dissolved metals (Cu, Zn)	234	50	$100	$ 28,400
dissolved organic carbon	234	34	$ 40	$ 10,720
total suspended sediment	234	0	$ 15	$ 3,510
hardness	234	34	$ 25	$ 6,700
			Total	$ 69,210
Atmospheric Deposition	**Samples**	**QA**	**Cost**	**Subtotal**
total metals (Cu, Zn)	12	46	$70	$ 4,060
dissolved metals (Cu, Zn)	12	46	$100	$ 5,800
dissolved organic carbon	12	34	$ 40	$ 1,840
total suspended sediment	12	0	$ 15	$ 180
hardness	12	34	$ 25	$ 1,150
			Total	$ 13,030
Teflon Liner	**Samples**	**QA**	**Cost**	**Subtotal**
total recoverable metals (Cu, Zn)	2	0	$70	$ 140
			Total	$ 140
Total				
			Lab Total	$ 82,380
			Supplies	$ 20,000
			Total	$102,380

6.0 Quality Objectives

6.1 Data quality objectives

To collect enough data of acceptable quality about the release of Cu and Zn from primary urban sources to meet the study objectives.

Monitoring activities conducted under this project will follow Ecology's standard operating procedures (SOPs). This project will not require additional data quality objectives (DQOs).

6.2 Measurement quality objectives

The measurement quality objectives (MQOs) for the analytical data in this study are detailed in Table 5.

MQOs for the two metals extraction methods are shown. The higher detection limit method will be used for initial metals sample analysis. If the preliminary Cu and Zn concentrations are below the higher detection limits, then subsequent samples will be analyzed with the lower detection limit method. The Cu and Zn data from both metals methods will only be used together if they are above the method detection limits for each respective method. Results below the method detection limits will not be included in any statistical analysis.

The MQOs for the comparison of field parameters (pH, conductivity, and turbidity) to calibration standards are provided in Table 6.

6.2.1 Targets for precision, bias, and sensitivity

6.2.1.1 Precision

Precision is a measure of the variability in the results of replicate measurements due to random error. Precision for two replicate samples is measured as the relative percent difference (RPD) between the two results. If there are more than two replicate samples, then precision is measured as the relative standard deviation (RSD).

Measurement quality objectives for the precision of laboratory duplicate samples and matrix spike duplicate samples are shown in Table 5.

6.2.1.2 Bias

Bias is the difference between the population mean and the true value. For this study, laboratory bias is measured as acceptable percent (%) recovery. Acceptance limits for laboratory verification standards, matrix spikes, and surrogate standards are shown in Table 5.

The bias associated with field measurements will be measured by daily instrument calibration checks using manufacturer recommended standard solutions. The instrument calibration readings will be compared to the field parameter MQOs to determine acceptable instrument bias (Table 6).

6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance above the background noise of the analytical system. Targets for sensitivity of field measurements and laboratory analyses, reporting limits (RLs), are described in Section 9.1.

Table 5. Laboratory measurement quality objectives.

MQO →	Precision		Bias			Sensitivity
Parameter	Duplicate Samples	Matrix Spike-Duplicates	Verification Standards (LCS,CRM,CCV)	Matrix Spikes	Surrogate Standards*	Method Detection Limit (MDL)
	Relative Percent Difference (% RPD)		Recovery Limits (%)			Units
Water Samples						
dissolved/total copper[1]	± 25%	70-130%	75-125%	± 25%	na	0.07 ug/L
dissolved/total zinc[1]	± 25%	70-130%	75-125%	± 25%	na	0.25 ug/L
dissolved/total copper[2]	± 25%	70-130%	75-125%	± 25%	na	0.016 ug/L
dissolved/total zinc[2]	± 25%	70-130%	75-125%	± 25%	na	0.092 ug/L
TSS	± 20%	na	80-120%	± 20%	na	1 mg/L
DOC	± 20%	na	75-125%	± 20%	na	0.1 mg/L
hardness	± 20%	75-125%	80-120%	± 25%	na	1 mg/L
Teflon Liner Samples						
metals	≤ 25%	70-130%	75-125%	≤ 25%	na	1 ug/g DW Cu 5 ug/g DW Zn

* Surrogate recoveries are compound specific.

[1] Metals detection limit for extraction and ICP-MS analysis by EPA200.8 methods

[2] Metals detection limit for extraction (EPA1640) and ICP-MS analysis (EPA200.8) methods

LCS: laboratory control sample
CRM: certified reference materials
CCV: continuing calibration verification standards
RPD: relative percent difference
TSS: total suspended solids
DOC: dissolved organic carbon
metals: total recoverable copper and zinc
na: not applicable

Table 6. Field parameter measurement quality objectives.

Parameter	Units	Accept	Qualify	Reject
pH	std. units	≤ ± 0.2	> 0.2 and ≤ 0.8	≥ ± 0.8
conductivity	uS/cm	≤ ± 5	> 5 and ≤ 15	≥ ± 15
turbidity	NTU	≤ ± 5	> 5 and ≤ 15	≥ ± 15

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

Use of SOPs will help ensure comparability of sampling and analysis between storm events as well as with many other stormwater studies. Section 8.1 lists the SOPs to be followed for field sampling.

6.2.2.2 Representativeness

Proper representativeness will be ensured by adhering to the approved SOPs and sampling protocols. Samples will be preserved and stored to ensure that lab holding conditions and times are met.

Representativeness will also be achieved by monitoring three locations for each Cu/Zn source during six different storm events. Monitoring locations will be selected to minimize contributions of Cu or Zn from other potential sources (e.g., HVAC units, roof vents, steel gutters). Other potential sources of Cu or Zn present will be noted and reported. In addition, monitoring sites with different aged building roofing and siding materials will be monitored to evaluate the impact of material age on Cu and Zn leaching.

Bulk atmospheric deposition samples will be collected at two locations within the study area for all storm events monitored. These samples will account for the Cu and Zn deposited onto the monitored materials by wet and dry atmospheric deposition. The atmospheric deposition stations will be located in the southwest and northeast quadrants of the study area. Deposition stations will be elevated on building roofs to reduce the possibility of sample contamination.

6.2.2.3 Completeness

The data for this project will be considered complete if 90% of the planned samples are collected and analyzed acceptably. If rainwater runoff monitoring is postponed due to an unusually dry year, then synthetic rainwater leaching events will substitute for the missing storm events.

6.3 Acceptance criteria for quality of existing data

The sources of Cu and Zn in the CuZn study area were evaluated and the variability of potential Cu and Zn released from each source assessed (Bookter, 2017). The urban sources with the highest potential to contribute Cu or Zn to the environment and the greatest variability around the estimated loading values were identified and recommended for monitoring. The variability of the estimated loading values is primarily due to the variability of the material release rates. The release rates used in Bookter (2017) were compiled from the Cu and Zn source literature.

The uncertainty of the loading estimates in Phase 1 of this study were evaluated using the coefficient of variance (CV). CV is a measure of the variation in a population of values around the mean. CV is calculated as the standard deviation divided by the mean (Miller and Miller, 2014). Bookter (2017) developed a qualitative uncertainty score for loading values, from the release rate literature, for comparison with CV (Table 7).

Table 7. Uncertainty classification system

Uncertainty Score	CV
Good	< 0.5
Fair	0.5-1.5
Poor	> 1.5

6.4 Model quality objectives

Not applicable to this study.

7.0 Study Design

7.1 Study boundaries

The CuZn study area is a portion of the lower Woodland Creek watershed in the City of Lacey and part of Thurston County. This area was selected for the concentrated commercial and industrial land use present (Section 3.2). Commercial and industrial areas have been shown to contribute higher Cu and Zn concentrations than other land uses (Norton et al., 2011; Hobbs et al., 2015). The sources of Cu and Zn in the built environment found in this study area should be representative of sources found in other commercial and industrial areas in Puget Sound.

The study area boundary was initially drawn along hydrological boundaries for two small watersheds draining into Woodland Creek. Since 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 (Figure 1).

7.2 Field data collection

The materials to be monitored in this project are summarized in the sampling plan (Table 8). The monitoring locations for each material type are given in Table 9.

7.2.1 Sampling locations and frequency

Rainwater runoff samples will be collected from four different types of roofing materials, three siding materials, roof gutters, chain-link fencing, and galvanized streetlight poles. Three monitoring sites will be sampled for each potential source of Cu and Zn. The runoff from each monitoring site will be sampled during six storm events. Old (>10 years) and new (<5 years) materials will be sampled for two roofing materials and one siding materials (Table 8).

In addition, the Teflon liners that will be used in the sample collection containers will be analyzed to determine the potential for liners to contaminate the collected samples with Cu or Zn.

Material type, brand, and age information will be collected from building construction and maintenance records. Material condition will be collected from Thurston County Assessor data and through onsite observation. This data will be used to indicate the variability of the materials monitored.

Table 8. Urban copper and zinc sampling plan

Source	Type	Age (years)	Sample Matrix	Number of Sites	Sample Events	Total Samples*
Rainwater Runoff						
Roofing	AAR	< 5	Water	3	6	18
Roofing	AAR	> 10	Water	3	6	18
Roofing	Metal	< 5	Water	3	6	18
Roofing	Metal	> 10	Water	3	6	18
Roofing	EPDM	-	Water	3	6	18
Roofing	TPO	-	Water	3	6	18
Gutters	Metal	-	Water	3	6	18
Siding	Fiber Cement	< 5	Water	3	6	18
Siding	Painted Wood	> 10	Water	3	6	18
Siding	Metal	< 5	Water	3	6	18
Siding	Metal	> 10	Water	3	6	18
Streetlight	Galvanized	-	Water	3	6	18
Chain-link Fence	Galvanized	-	Water	3	6	18
Atmospheric Deposition						
Atmospheric Deposition	Bulk	-	Water	2	6	12
Teflon Liner						
Liner	MPTFE Teflon	-	solid	-	1	1
Liner	PFA Teflon	-	solid	-	1	1
Total				**41**	**6**	**248**

** Not including quality assurance (QA) samples.*
AAR = asphalt shingle with algae-resistant granules, Metal = painted steel.
EPDM = ethylene propylene terpolymer, TPO = thermoplastic polyolefin.
MPTFE = modified polytetrafluoroethylene, PFA = perfluoroalkoxy.

Monitoring locations are selected based on the type of construction material, material age, the logistical convenience for sample collection, and the ability to isolate that material from other sources of Cu and Zn. Isolating materials from other potential sources may be difficult. For example, building roofs are often comprised of the roofing materials, HVAC units, guardrails, flashing, and vents. All these roof components can be sources of Cu or Zn. Sample locations on each building are selected to minimize the presence of other potential sources of Cu or Zn. All potential sources will be surveyed and reported to indicate the potential for additional contributions of Cu and Zn. The analytical results from this approach will provide an overview of Cu and Zn contributions from whole roof and siding systems.

Roof monitoring sites with aluminum gutters and downspouts are given preference. Aluminum gutters are not a potential source of Cu and Zn, since aluminum is not comprised of Cu or Zn. For roofs with aluminum gutters, aluminum downspout diverters will be installed in gutter downspouts to route rainwater runoff into 55-gallon sample collection drums. The collection drums will be lidded with only a small opening for the downspout diverter to ensure that only rainwater from the roofing material is collected. This method of sample collection will provide a convenient and safe method of sample collection by limiting the need to access building roofs during sample processing.

Most low-slope, commercial roofs in the CuZn study area are drained via polyvinyl chloride (PVC) or galvanized steel downspouts. PVC and galvanized drain pipes are potential sources of Cu and Zn. Rainwater will be monitored from low-sloped roofs with PVC or galvanized downspouts by plugging one roof drain, using a stainless steel or aluminum plug, and collecting grab samples from the ponded stormwater. Roof sections will be selected to minimize the contribution of Cu or Zn from other roof components. Ethylene propylene diene terpolymer (EPDM) and thermoplastic polyolefin (TPO) are low-slope roofing materials that will be monitored in this study.

Table 9. Proposed monitoring locations.

Material Information			Location Information		
Source	**Type**	**Age**	**Latitude**	**Longitude**	**Address**
Roofing	AAR	1	47.05574	-122.75723	8515 Litt Dr NE
Roofing	AAR	3	47.06177	-122.88280	1511 Miller Ave NE; Olympia
Roofing	AAR	4	47.03957	-122.79380	6729 Pacific Ave SE
Roofing	AAR	10	47.05526	-122.78624	1210 Neil St NE
Roofing	AAR	13	47.06949	-122.77978	2400 Callison Rd NE
Roofing	AAR	19	47.05598	-122.76355	130 Marvin Rd SE
Roofing	Metal	<1	47.03787	-122.89767	1111 Washington St SE; Olympia
Roofing	Metal	2	47.04982	-122.83319	250 Sleater Kinney Rd NE
Roofing	Metal	4	47.06924	-122.77188	2527 Marvin Rd NE
Roofing	Metal	12	47.07607	-122.75064	3020 Willamette Dr NE
Roofing	Metal	12	47.04840	-122.80121	6121 Martin Way E
Roofing	Metal	30	47.06063	-122.79736	1415 Sandy Ln NE
Roofing	EPDM	3	47.03716	-122.89671	1111 Washington St SE; Olympia
Roofing	EPDM	18	47.05728	-122.76604	8230 Martin Way E
Roofing	EPDM	24	47.04752	-122.80779	300 Desmond Dr SE
Roofing	TPO	4	47.06920	-122.77181	2527 Marvin Rd NE
Roofing	TPO	8	47.08516	-122.83544	3845 Sleater Kinney Rd NE; Olympia
Roofing	TPO	10	47.03472	-122.90517	504 15th Ave SE; Olympia
Siding	Fiber Cement	1	47.08194	-122.75358	8850 Adonis Ct NE
Siding	Fiber Cement	4	47.07777	-122.78585	3061 Eagle Lp NE
Siding	Fiber Cement	5	47.08915	-122.75809	4089 Campus Willows Lp NE
Material Information			**Location Information**		

Material Information			Location Information		
Source	**Type**	**Age**	**Latitude**	**Longitude**	**Address**
Source	**Type**	**Age**	**Latitude**	**Longitude**	**Address**
Siding	Painted Wood	12	47.07583	-122.75041	3020 Willamette Dr NE
Siding	Painted Wood	14	47.05518	-122.78636	1210 Neil St NE
Siding	Painted Wood	29	47.06178	-122.88303	1511 Miller Ave NE; Olympia
Siding	Metal	1	47.07196	-122.76820	8276 28th Ct NE
Siding	Metal	2	47.04961	-122.83316	250 Sleater Kinney Rd NE
Siding	Metal	4	47.06935	-122.77183	2527 Marvin Rd NE
Siding	Metal	12	47.04752	-122.81003	300 Desmond Dr SE
Siding	Metal	16	47.05974	-122.75368	8770 Tallon Ln NE
Siding	Metal	30	47.06053	-122.79743	1415 Sandy Ln NE
Gutters	Metal	<1	47.03787	-122.89767	1111 Washington St SE; Olympia
Gutters	Metal	4	47.06930	-122.77190	2527 Marvin Rd NE
Gutters	Metal	12	47.04840	-122.80121	6121 Martin Way E
Streetlight	Galvanized	8	47.04961	-122.81632	-
Streetlight	Galvanized	>30	47.04931	-122.81673	-
Streetlight	Galvanized	>30	47.06296	-122.76324	-
Chain-link	Galvanized	7	47.07248	-122.76893	8270 28th Ct NE
Chain-link	Galvanized	8	47.04938	-122.81638	-
Chain-link	Galvanized	>11	47.08522	-122.83550	3845 Sleater Kinney Rd NE
Atmospheric Deposition		-	47.04773	-122.80829	300 Desmond Dr SE
Atmospheric Deposition		-	47.07212	-122.76750	8284 28th Ct NE

All monitoring sites located in Lacey, Washington unless noted.
** Monitoring location identified, waiting for site information.*
AAR = asphalt shingle with algae-resistant granules, Metal = painted steel.

EPDM = ethylene propylene terpolymer, TPO = thermoplastic polyolefin.

Building siding locations are selected to maximize rainwater volume and reduce the Cu and Zn contributions from other construction materials. Building siding facing the prevailing weather direction will be monitored when possible. This face of a building should be impacted by more rainwater runoff then the other sides of the building. The majority of storms in the CuZn study area come from the southwest. Siding material locations will be selected where the building siding does not collect direct roof runoff (e.g., below the roof drip line or leaking gutters).

Rainwater from building siding will be collected by one of two sample collection systems. (1) An aluminum pan will be placed beneath the siding drip line. The pan will be lidded with only the area underneath the dripline open for rainwater collection. (2) Installing aluminum or weather strip diversion structures near the base of building walls. The diversions will direct rainwater runoff into an aluminum or stainless steel funnel. The funnel will deliver the rainwater into a 5-gallon sample collection container. The collection container will be lidded with only a small opening for the funnel to ensure that only rainwater from the siding material is collected.

Building siding made of painted wood installed in the last 5 years is uncommon. An initial survey indicates that newer painted wood siding is not widely used and therefore is likely not a major contributing source of Cu and Zn. The majority of new homes are constructed with fiber cement siding. Fiber cement siding that was installed in the last 5 years has been included as one of the building materials that will be monitored. It is a relatively new construction material with limited information about its potential to release Cu and Zn to the environment.

The contribution of Cu and Zn from painted steel gutters will be calculated as the difference between the total roof runoff (i.e., roofing and gutters) and the rainwater runoff from the roofing material alone. The two samples will be collected from different locations on the same roof system. The roof material runoff will be isolated using an aluminum or weather strip diversion installed above the roof gutter system and directing runoff into a separate aluminum downspout. The total roof runoff sample will collect the accumulated runoff at the base of the gutter downspout after the rainwater has interacted with the roofing material, gutter, and downspout. The Cu and Zn contribution of the gutter and downspout will be calculated by subtracting the roofing material runoff concentrations from the concentrations in the total roof runoff.

Rainwater from galvanized streetlight poles will be collected by installing an aluminum foil collar near the base of the pole. The collar will route rainwater runoff into an aluminum or stainless steel funnel. The funnel will deliver the rainwater into a 5-gallon sample collection container. The collection container will be lidded with only a small opening for the funnel to ensure that only rainwater from the streetlight pole is collected.

Rainwater from galvanized chain-link fence will be collected in an aluminum or stainless steel pan placed below a section of fence. The pan will be lidded on either side of the fence to ensure that only rainwater that has interacted with the chain-link material is collected.

Bulk atmospheric deposition samples will be collected at two sites in the CuZn study area and will be collected for each storm event monitored. The atmospheric deposition stations will be located in the southwest and northeast quadrants of the study area (Table 9). Deposition stations will be elevated on building roofs to reduce the possibility of sample contamination.

For a storm to qualify as a valid storm event, it must have a minimum rainfall depth of 0.2 inches and be preceded by an antecedent dry period of 6 hours. Precipitation data from the Thurston County Waste and Recovery Center meteorological station (Thurston, 2017) and forecasts from online weather services will be used to select appropriate storm events for monitoring. For this study, an antecedent dry period is a period of time with less than 0.02 inches of rainfall.

Synthetic rainwater leaching may be used to replace missing storm events. Leaching will be accomplished by washing monitoring site surfaces with a chemical mixture with a pH similar to natural rainwater. Leaching will only be performed when not enough storm events with the minimum rainfall depth occur during the sampling season.

7.2.2 Field parameters and laboratory analytes to be measured

Rainwater runoff samples will be analyzed for total and dissolved metals (Cu, Zn), dissolved organic carbon (DOC), water hardness, and total suspended sediment (TSS). In addition, the pH,

conductivity, and turbidity of the water samples will be measured using a field-deployed instrument.
Bulk atmospheric deposition samples will be analyzed for the total and dissolved metals (Cu, Zn). If sufficient sample volume is collected, then atmospheric deposition samples will also be analyzed for DOC, water hardness, pH, conductivity, and turbidity. These supplemental bulk atmospheric deposition parameters are listed in order of priority.

Initially, all metals samples will be extracted and analyzed by ICP-MS following the protocols outlined in EPA method 200.8. If the Cu and Zn concentrations from the first stormwater event are below the method detection limit, then the remaining storm event metals analyses will be performed using the more sensitive, lower detection limit, method (EPA1640/EPA200.8).

Teflon liner samples will be analyzed for total recoverable metals (Cu, Zn) before being used in the sample collection containers. There are two types of Teflon liner available: modified polytetrafluoroethylene (MPTFE) and perfluoroalkoxy (PFA). The analytical results for the Teflon liners will indicate whether the Teflon liner materials are a potential source of Cu or Zn. If Cu or Zn is present in the liners, then an alternative liner material will be sought.

7.3 Modeling and analysis design

Not applicable to this study.

7.4 Assumptions in relation to objectives and study area

The main assumptions for Phase 2 of the CuZn study are summarized below.

- The quantity of Cu and Zn leached from the materials monitored is representative of all similar materials in the study area.
- Based on previous study results, Cu and Zn concentrations will be detectable in stormwater runoff from construction materials.
- The metals concentrations at two bulk atmospheric deposition sites in the study area accurately represent the quantity of Cu and Zn deposited on building materials throughout the study area.
- The precipitation data collected at the Thurston County Waste and Recovery Center are representative of precipitation data throughout the study area.
- Synthetic rainwater washoff of construction materials will simulate the leaching process of natural storm events. This method was used in a study analyzing metal leaching from building siding at the University of Maryland (Davis et al., 2001).

7.5 Possible challenges and contingencies

The goal of this project is to measure the quantity of Cu and Zn released from potential sources of those metals in the urban environment. The monitoring plan described in this QAPP is designed to capture rainwater runoff from materials installed in the built environment and to collect samples that incorporate the variability in construction materials and climate. Collecting rainwater samples that are representative of actual conditions in the environment always involves challenges and logistical problems.

7.5.1 Logistical problems

The potential logistical problems (•) and related contingencies plans (✓) are listed below.

- Capturing six storm events with sufficient rainfall depth and preceding dry period.
  - ✓ The precipitation data collected in the CuZn study area will be tracked (Thurston, 2017) and compared with precipitation data from online weather forecasts (NWS, 2017; Wunderground, 2017).
  - ✓ Substitute synthetic rainwater leaching during dry weather for missing storm events.
- Ensure that all the rainwater runoff from a material surface is captured.
  - ✓ Each material surface area will be isolated by selecting monitoring sites where all stormwater runoff is collected at one point.
  - ✓ If necessary, temporary flow guidance structures will be installed during the sampling season (e.g., check dams using weather stripping materials, aluminum foil collars around the base of streetlight poles).
- Rainfall does not make sufficient contact with building siding materials.
  - ✓ Relocate sample collection system.
  - ✓ Substitute synthetic rainwater leaching for storm events where siding is not impacted by rainwater runoff.
- Limit direct rainfall into sample collection containers.
  - ✓ Collect rainwater in lidded containers (e.g., buckets, drums).
  - ✓ Use funnels (e.g., aluminum gutter downspout material, stainless steel funnel) to plumb runoff water from stormwater collection systems to lidded sample containers.
- Overflow of sample collection containers.
  - ✓ Size collection containers for expected runoff volumes.
  - ✓ Invalidate samples from overflow events. Do not analyze.
  - ✓ Increase volume of collection container for later storm events.
- Collect sufficient bulk atmospheric deposition sample to analyze for all analytical parameters.
  - ✓ Use atmospheric deposition collection funnels with an 18 inch diameter.
  - ✓ When possible, target storm events with more than 0.3 inches of rainfall.
  - ✓ Rinse sample collection container with deionized water, combine rinsate water with total sample volume, and record rinsate volume to account for resultant dilution.
- Access to sufficient monitoring sites is unavailable.
  - ✓ Incorporate monitoring sites close to, but outside of, the study area boundary.
- Roof access with fall hazards.
  - ✓ Train staff in proper fall protection methods.
  - ✓ Provide fall protection equipment.

7.5.2 Practical constraints

The Cu and Zn concentrations in rainwater and atmospheric deposition samples may be lower than the normal metal analysis method detection (EPA200.8). If preliminary results indicate this is an issue, then a more accurate metal analysis method (EPA1640/EPA200.8) will be used. The analytical cost of the lower detection limit metals method may require additional laboratory budget and the monitoring of fewer sampling events.

Rainwater runoff will be collected and stored during storm events. Samples will be processed for delivery to the laboratory within 24 hours of the end of the storm event. Sample preservation will be performed at the time of sample processing.

7.5.3 Schedule limitations

The sample schedule (Table 2) is designed to accommodate sampling delays.

It is possible that not enough storm events with sufficient rainfall will occur during the sampling period. If this situation arises, then synthetic rainwater leaching events will be sampled instead of storm events to keep the project on schedule.

8.0 Field Procedures

8.1 Invasive species evaluation

Field personnel for this project are required to be familiar with and follow the procedures described in *Minimizing the Spread of Invasive Species* (Parsons et al., 2012). The collection of rainwater runoff from materials in the built environment has limited potential to spread invasive species to aquatic environments.

8.2 Measurement and sampling procedures

The standard operating procedures (SOPs) followed during this project are listed below.

- ECY001 – *Collecting Grab Samples from Stormwater Discharges* (Lowe et al., 2009).
- EAP029 – *Collection and Field Processing of Metals Samples, version 1.5* (Ward, 2015).
- EAP031 – *Collection and Analysis of pH Samples, version 1.4* (Ward, 2014).
- EAP032 – *Collection and Analysis of Conductivity Samples, version 2.2* (Ward, 2014).
- EAP070 – *Minimizing the Spread of Invasive Species* (Parsons et al., 2012).
- EAP090 – *Decontaminating Field Equipment for Sampling Toxics in the Environment* (Friese, 2014).
- *Environmental Assessment Program Safety Manual* (Ecology, 2017).

The monitoring of Cu and Zn released from construction materials will be performed following the procedure outlined below. Details related to each sample collection step are provided in the following sections (8.2.1 to 8.2.3).

1. Rainwater runoff collection

Rainwater runoff samples will be collected for six storm events with a minimum rainfall depth of 0.2 inches and a preceding antecedent dry period of 6 hours. Passive collection systems will collect and store the runoff during the storm event. Stormwater samples will be collected within 24 hours of the end of each sampled storm event.

2. Atmospheric deposition collection

The bulk atmospheric deposition collection systems will be deployed during each sampled stormwater event and the preceding antecedent dry period. This will allow the collection of the wet and dry deposition related to each sampled storm event.

3. Synthetic rainwater leaching

If necessary, the materials at each monitoring site will be washed with synthetic rainwater and the washoff samples collected for analysis. This leaching will be performed in place of storm events in the following scenarios.

- Not enough storm events are captured with sufficient rainfall depth.
- Very little rainfall impacts building siding materials.

All samples collected will follow the preservation and holding time guidelines in Table 10. All personnel will wear non-talc, nitrile gloves while collecting and processing samples.

8.2.1 Rainwater runoff collection

Rainwater runoff samples will be collected and stored by passive sample collection systems. The basic design of the passive sample collection systems for the different material types are described in section 7.2.1.

In general, rainwater will be diverted from materials of interest using stainless steel or aluminum materials and funnels and collected in Teflon lined containers. The sample containers will be sized to accommodate the expected runoff volume at each monitoring site. Coarse stainless steel filters will be used inside the funnels to remove large debris (e.g., pine cones, needles, and twigs) from the collected sample. For low-sloped roofs, a roof drain will be plugged and the ponded water sampled. Small variations in these designs may be necessary depending on site conditions. The various collection systems used in this study will be detailed in the final report.

Rainwater runoff samples will be collected within 24 hours of the end of the storm event. The total collected sample will be homogenized by agitation of the sample inside of the Teflon liner or by stirring with an acid-washed mixing rod. Aliquots of the bulk sample will be separated into individual analyte bottles for transport to the laboratory. The remaining sample will be analyzed in the field for pH, conductivity, and turbidity.

Rainwater runoff samples will be analyzed by Manchester Environmental Laboratory (MEL) for total and dissolved metals (Cu, Zn), dissolved organic carbon (DOC), total suspended sediment (TSS), and water hardness.

Filtering for dissolved metals and dissolved organic carbon will be conducted on-site within 15 minutes of sample processing using pre-cleaned 0.45 um filters. The first few milliliters of filtrate will be discarded.

All components of the passive sample collection systems will be acid-washed prior to the first use (see section 8.4).

8.2.2 Atmospheric deposition collection

Atmospheric deposition collection systems will be deployed during each monitored storm event and the preceding antecedent dry period. This will allow the collection of both wet and dry deposition related to each sampled storm event. The collection systems will be removed from the rooftops during minor precipitation events to eliminate the collection of wet deposition during those storms. If rainwater is collected outside of a monitored storm event, then the collection system will be acid-washed before redeployment (section 8.4). Atmospheric deposition samples will be processed using the same methods as the rainwater runoff samples.

Bulk atmospheric deposition samples will be collected using a stainless steel funnel draining into a 5-gallon bucket lined with a Teflon bag. The funnel will have an 18 inch diameter circular opening exposed to the atmosphere. This collection system is designed from a similar system used on the Spokane River (Era-Miller and Wong, 2016).

The quantity of rainwater collected during a 0.2 inch or greater storm should provide sufficient atmospheric deposition sample volume for both total and dissolved metal analysis. The minimum sample volume required for total and dissolved metals analysis is 700 mL for normal metals analysis detection limits. An estimated rainfall volume of 800 mL will be collected by an 18-inch diameter atmospheric deposition collection funnel from 0.2 inches of rainfall. When possible, storm events with more than 0.2 inches of rainfall will be monitored.

The atmospheric deposition collection systems will be acid-washed (section 8.4) prior to deployment.

8.2.3 Synthetic rainwater leaching

Synthetic rainwater leaching will be performed to replace any missing storm events or when not enough rainwater volume impacts building siding materials. Leaching samples will be collected using the same sample collection systems used for the rainwater runoff samples (section 8.2.1).

The leaching samples will be analyzed for total and dissolved metals (Cu, Zn), DOC, TSS, water hardness, pH, conductivity, and turbidity.

Construction materials will be washed with a known volume of synthetic rainwater. The volume of synthetic rainwater will be dependent on the surface area of the material being washed.

The synthetic rainwater mixture used for washing down material surfaces will be created from deionized water, nitric acid (HNO_3), sulfuric acid (H_2SO_4), and sodium chloride (NaCl). The pH of the synthetic rainwater will have a pH of approximately 5.1, similar to the pH of natural rainwater in western Washington (NTN, 2017). Davis et al. (2001) used a synthetic rainwater with pH between 4.2 and 4.4, made up of 23 micromoles (uM) NaCl, 18 uM HNO_3, and 18 uM H_2SO_4.

If synthetic rainwater is produced for this study, then two quality control tests will be performed.

- Blank synthetic rainwater will be analyzed for total and dissolved metals (Cu, Zn) for 10% of the batches used during the project. If only one batch is produced, then that batch will be analyzed.
- To test for leaching of metals from the Teflon liners, a blank synthetic rainwater sample will be stored in a Teflon liner for 24 hours and analyzed for total and dissolved metals (Cu, Zn).

8.3 Containers, preservation methods, holding times

Table 10. 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 um filter	Filter, 1:1 HCl ≤ 6 °C	28 days
total suspended sediment	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
total recoverable metal	sediment	50 g	4 oz glass gar	≤ 6 °C	6 months
total organic carbon	sediment	25 g	2 oz glass jar	≤ 6 °C	14 days

*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.

8.4 Equipment decontamination

Passive sample collection containers (e.g., buckets, drums) will be lined with new Teflon bags for each sampling event. Liners will be analyzed before use to ensure no potential Cu or Zn contamination from the liners.

All reusable sampling equipment (e.g., mixing rods, atmospheric deposition funnels) will be cleaned and acid-washed prior to each storm deployment. The cleaning procedure includes the following steps: clean with warm soapy water, rinse with deionized water, rinse with 10% high-purity nitric acid, and rinse with deionized water.

The decontamination procedure for metal analysis is described in further detail in *Decontamination of Sampling Equipment for Use in Collecting Toxic Chemical Samples* (Friese, 2014).

8.5 Sample ID

Laboratory sample IDs will be assigned by Manchester Environmental Laboratory (MEL).

8.6 Chain-of-custody

Chain-of-custody will be maintained for all samples throughout the project. The Laboratory Analysis Required (LAR) form provided by MEL will be used to track sample chain-of-custody.

8.7 Field log requirements

The following information will be recorded in the project field log:

- Name and location of project
- Material type
- Field personnel
- Sequence of events
- Any changes or deviations from the QAPP
- Environmental conditions
- Date, time, location, ID, and description of each sample
- Field instrument calibration procedures
- Field measurement results
- Identity of QC samples collected
- Presence of other potential sources of Cu or Zn
- Presence or absence of oil sheen
- Unusual circumstances that might affect interpretation of results

8.8 Other activities

Not applicable. Required activities are described in other sections of this QAPP.

9.0 Laboratory Procedures

9.1 Lab procedures table

Table 11. Measurement methods (laboratory).

Analyte	Sample Matrix	Samples*	Expected Range of Results	Reporting Limit	Sample Prep Method	Analytical (Instrument Method)
Water Samples						
dissolved / total copper	water	574	MDL – 8,000	0.1 ug/L	EPA 200.8	EPA 200.8
dissolved / total zinc	water	574	MDL – 15,000	5.0 ug/L	EPA 200.8	EPA 200.8
dissolved / total copper	water	574	MDL – 8,000	0.05 ug/L	EPA 1640	EPA 200.8
dissolved / total zinc	water	574	MDL – 15,000	0.2 ug/L	EPA 1640	EPA 200.8
dissolved organic carbon	water	574	1 – 50	1 mg/L	na	SM5310B
total suspended sediment	water	574	1 – 10	1 mg/L	na	SM2540 D-97
hardness as $CaCO_3$	water	574	0.5 – 50	0.33 mg /L	na	EPA 200.7
Teflon Liners						
total recoverable copper	solid	2	5 – 100	5.0 ug/g	EPA 3050B	EPA 6020B
total recoverable zinc	solid	2	5 – 600	0.1 ug/g	EPA 3050B	EPA 6020B

* Number of water samples includes QA samples and is dependent on preliminary metal results
MDL = method detection limit
EPA = Environmental Protection Agency
SM = Standard Method
PSEP = Puget Sound Estuary Program
na = not applicable

Table 12. Measurement methods (field equipment).

Analyte	Sample Matrix	Expected Range	Reporting Limit*	Analytical (Instrument Method)
pH	Water	5 – 9	0.01	pH sensor
conductivity	Water	5 – 5,000	0.01 uS/cm	conductivity sensor
turbidity	Water	0.5 - 500	0.1 NTU	turbidity sensor

* Reporting limits based on YSI EXO and ProDSS sensors

9.2 Sample preparation methods

All rainwater runoff, atmospheric deposition, and leaching samples will be collected from each sampling event and stored in Teflon lined sample containers until the event is complete. Sampling personnel will homogenize the bulk samples by agitation of the sample inside of the Teflon liner or by stirring with an acid-washed mixing rod. Aliquots of the bulk sample will be separated into individual analyte bottles for transport to the laboratory. Quality control samples (field blanks, field duplicates, matrix spike, and matrix spike duplicates) will also be collected in the appropriate analyte bottles at this time. All sample bottles will be labeled.

Dissolved metal and dissolved organic carbon samples will be filtered in the field using pre-cleaned 0.45 um pore size filters.

Teflon liner samples will be collected in glass jars for transport to the laboratory.

All samples will be preserved with appropriate preservatives (Table 10) and kept on ice, or in a refrigerator, until analyzed.

9.3 Special method requirements

Not applicable to this project.

9.4 Laboratories accredited for methods

All analyses will be carried out at Manchester Environmental Laboratory.

10.0 Quality Control Procedures

10.1 Table of field and laboratory quality control

All quality control (QC) procedures will follow the measurement quality objects (MQOs) detailed in Section 6.2 of this QAPP.

Table 13. Quality control samples, types, and frequency.

Parameter	Field		Laboratory			
	Blanks	Replicates	Check Standards	Method Blanks	Analytical Duplicates	Matrix Spikes
Water Samples						
metals	1/batch	1/batch	1/batch	1/batch	1/batch	1/batch
dissolved organic carbon	-	-	1/batch	1/batch	1/batch	1/batch
total suspended sediment	-	-	1/batch	1/batch	1/batch	-
hardness as CaCO3	-	-	1/batch	1/batch	1/batch	1/batch
Atmospheric Deposition						
metals	1/batch	1/batch	1/batch	1/batch	1/batch	1/batch
dissolved organic carbon	-	-	1/batch*	1/batch*	1/batch	1/batch
total suspended sediment	-	-	1/batch*	1/batch*	1/batch	-
hardness as CaCO3	-	-	1/batch*	1/batch*	1/batch	1/batch
Synthetic Rainwater						
metals	10% **	-	-	-	-	-
total organic carbon	-	-	-	-	-	-
Teflon Liners						
metals	-	-	1/batch	1/batch	1/batch	-

* 1/batch, if sufficient sample volume is collected
** 10% of the batches of synthetic rainwater produced will be tested for metals.

Equipment blanks will be performed on the atmospheric deposition collection system, aluminum collection pans, and Teflon liners. One of the two atmospheric deposition collection systems will have equipment blanks sampled before each of the six sample events. The deposition collection system sampled for an equipment blank will alternate between sample events. This will result in each deposition collection system having an equipment blank performed during every other sample event. One equipment blank will be collected from a 5-gallon Teflon bucket liner and an aluminum collection pan during the first sample event.

Field blanks will be performed on the Nalgene filter apparatus used to filter dissolved metals samples. The Nalgene filter apparatus is made of high density polyethylene plastic and may be a source of Zn. Eight field blanks will be collected from the dissolved metals filter apparatus during the six sample events: two during the first sample event, two during the second sample event, and one for each of the remaining four sample events.

The equipment and field blanks will be performed by rinsing the equipment with laboratory provided deionized water and collecting the resultant rinsate before sample collection or filtration. The atmospheric deposition collection system equipment blanks will be analyzed for total and dissolved metals (Cu, Zn). The dissolved metals filter apparatus field blanks will be analyzed for dissolved metals (Cu, Zn).

The field-deployed water quality sensors (pH, conductivity, and turbidity) will be calibrated before each sample collection event and checked against calibration standards at the end of each event. Conductivity and turbidity sensors are very stable. If the standard check before a sample event is within MQOs (Table 6), then the conductivity and turbidity sensors will not be calibrated for that day. The pH sensor will be calibrated with a 3-point calibration with standards for pH 4, 7, and 10 for every sample event. The conductivity sensor will have a 1-point calibration performed with a 1,000 uS/cm standard. The turbidity sensor will have a 3-point calibration with 0 NTU (deionized water), 126 NTU, and 1010 NTU standards. All standard solutions used will be manufacturer recommended standards.

10.2 Corrective action processes

The laboratory analysts will document whether project data meets method QC criteria. Any departures from normal analytical methods will be documented by the laboratory and described in the data package from the laboratories and also in the final report for the project. If any samples do not meet QC criteria, then the project manager will determine whether the analytical data should be re-analyzed, rejected, or used with appropriate qualification.

Field instruments will be calibrated and checked against standards for every sample event. The start and end of the event standard checks of the instrument should be within the MQOs defined in Table 6. If any of the field measurement data do not meet QC criteria, then the project manager will determine whether field instrument data should be rejected or used with appropriate qualification.

Teflon liners will be analyzed for total recoverable metals (Cu, Zn) before use. If the results indicate the presence of Cu or Zn, then an alternative sample collection container liner will be sought.

11.0 Management Procedures

11.1 Data recording and reporting requirements

Field data will be recorded in a bound, waterproof notebook on Rite in the Rain paper. Corrections will be made with single line strikethroughs and initialed. Data will be transferred to Microsoft Excel for creating data tables.

Field and laboratory data for the project will be entered into Ecology's EIM system.

11.2 Laboratory data package requirements

The laboratory data package will be generated by Manchester Environmental Laboratory (MEL). MEL will provide a project data package that will include: a narrative discussing any problems encountered in the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. Quality control results will be evaluated by MEL (discussed below in *Section 13.0 Data Verification*).

The following data qualifiers will be used:

- "J" – The analyte was positively identified. The associated numerical result is an estimate.
- "UJ" – The analyte was not detected at or above the estimated reporting limit.
- "U" – The analyte was not detected above the reporting limit.
- "NJ" – The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.

The qualifiers will be used in accordance with the method reporting limits such that:

- For non-detect values, the estimated detection limit (EDL) is recorded in the "Result Reported Value" column and a "UJ" in the "Result Data Qualifier" column.
- Detected values that are below the quantitation limits (QL) are reported and qualified as estimates ("J").

11.3 Electronic transfer requirements

All laboratory data will be accessed and downloaded from MEL's Laboratory Information Management System (LIMS) into Excel spreadsheets. MEL will provide an electronic data deliverable (EDD).

11.4 EIM/STORET data upload procedures

All completed project data will be entered into Ecology's Environmental Information Management (EIM) database. Data entered into EIM follow a formal data review process where data are reviewed by the project manager, the person entering the data, and an independent reviewer.

EIM can be accessed on Ecology's Internet homepage at http://www.ecy.wa.gov/eim/.

The data from this project will be searchable under Study ID ABOO0001.

11.5 Model information management

Not applicable to this project.

12.0 Audits and Reports

12.1 Field, laboratory, and other audits

No defined audit exists for the field work in this project.

Ecology's Environmental Laboratory Accreditation Program evaluates a laboratory's quality system, staff, facilities and equipment, test methods, records, and reports. It also establishes that the laboratory is capable of providing accurate, defensible data. All assessments are available from Ecology upon request, including MEL's internal performance and audits.

12.2 Responsible personnel

The project manager will be responsible for all reporting.

12.3 Frequency and distribution of reports

One final report will be published at the end of the project summarizing the results and comparing them with the Phase 1 results for the CuZn study. The National Estuary Program (NEP) quality coordinator will review and comment on a draft of the final report.

12.4 Responsibility for reports

The report will be authored by the project manager.

13.0 Data Verification

13.1 Field data verification, requirements, and responsibilities

Field data verification will be conducted by the project manager.

13.2 Laboratory data verification

Data verification involves examining the data for errors, omissions, unusual or outlier values, and compliance with QC acceptance criteria. MEL's SOPs for data reduction, review, and reporting will meet the needs of the project.

MEL staff will provide a final written report of their data review which will include a discussion of whether (1) MQOs were met, (2) proper analytical methods and protocols were followed, (3) calibrations and controls were within limits, and (4) data were consistent, correct, and complete, without errors or omissions.

The principal investigator/project manager is responsible for the final acceptance of the project data. The complete data package, along with MEL's written report, will be assessed for completeness and reasonableness. Based on these assessments, the data will either be accepted, accepted with qualifications, or rejected and re-analysis considered.

Accuracy of data entered into EIM will be verified by someone other than the data engineer per EIM data entry business rules.

13.3 Validation requirements, if necessary

Independent data validation will not be required for this project.

13.4 Model quality assessment

Not applicable for this project.

14.0 Data Quality (Usability) Assessment

14.1 Process for determining project objectives were met

The project manager will determine if the project data are useable by assessing whether the data have met the MQOs outlined in Tables 5, 6, 11, and 12. Based on this assessment, the data will either be accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

14.2 Treatment of non-detects

Laboratory data will be reported down to the method detection limit, with an associated "U" or "UJ" qualifier for non-detects. Statistical tests requiring substitution for non-detects will not be included in the published report. Summed values will include only detected concentrations.

If initial results indicate numerous non-detect data, then alternate analytical methods with lower detection limits will be used for the remaining samples.

14.3 Data analysis and presentation methods

A summary of the data will be presented in the final report.

Metals concentrations will be used to calculate Cu and Zn release rates using the mass of metal, surface area of contributing source material, and storm event rainfall depth. The method for calculating annual release rates is described in the Phase 1 report (Bookter, 2017).

The release rates developed from the whole roofing and siding systems monitored in this study will be representative of all potential sources of Cu and Zn on those systems. The presence of other potential sources (e.g., HVAC units, galvanized vents) will be noted in the final report.

14.4 Sampling design evaluation

Three sample sites per material type is a minimum for basic statistical analyses (e.g., minimum, mean, and maximum). Comparison of metals released by different aged materials will be performed using non-parametric analysis of variance tests (e.g., Mann-Whitney U test). Sampling six storm events will allow for a more robust assessment of variability for each material type (e.g., minimum, median, mean, standard deviation, and maximum). The uncertainty of the release rates developed from the results of this study will be evaluated using the coefficient of variation (section 6.3).

14.5 Documentation of assessment

The final report will present the findings, interpretations, and recommendations from this study. It will be reviewed by the National Estuary Program (NEP) Quality Coordinator and by an Ecology peer before it is finalized.

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16.0 Appendix. Glossaries, Acronyms, and Abbreviations

Glossary of General Terms

Bulk atmospheric deposition: The combination of wet and dry particles deposited on buildings and land surfaces from the atmosphere.

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.

Effluent: An outflowing of water from a natural body of water or from a human-made structure. For example, the treated outflow from a wastewater treatment plant.

Leachate: Liquid that has flowed over, or percolated through, a solid and leached some of the material constituents. For the CuZn study, synthetic rainwater may be used to produce construction material leachates.

Load allocation: The portion of a receiving water's loading capacity attributed to one or more of its existing or future sources of nonpoint pollution or to natural background sources.

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

Rainwater Runoff: Precipitation that falls on and flows over constructed surfaces.

Rinsate: Blank water that has flowed over (i.e., rinsed) a container or sample equipment.

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.

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.

Acronyms and Abbreviations

AAR	Asphalt Shingles with Algae-resistance, a roofing material
BMP	Best management practice
Cu	Copper
DOC	Dissolved organic carbon
e.g.	For example
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
EPDM	Ethylene Propylene Terpolymer, a roofing material
et al.	And others
GIS	Geographic Information System software
i.e.	In other words
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
QA	Quality assurance
QC	Quality control
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedure
TOC	Total organic carbon
TPO	Thermoplastic polyolefin, a roofing material
TSS	(See Glossary above)
WRIA	Water Resource Inventory Area
Zn	Zinc

Units of Measurement

°C	degrees centigrade
°F	degrees fahrenheit
ft	feet
g	gram, a unit of mass
kg	kilograms, a unit of mass equal to 1,000 grams
m	meter
mg	milligram
mg/L	milligrams per liter (parts per million)
mL	milliliter
s.u.	standard units
ug	microgram
ug/g	micrograms per gram (parts per million)
ug/L	micrograms per liter (parts per billion)
uS/cm	microsiemens per centimeter, a unit of conductivity

Quality Assurance Glossary

Accreditation: A certification process for laboratories, designed to evaluate and document a lab's ability to perform analytical methods and produce acceptable data. For Ecology, it is "Formal recognition by (Ecology)…that an environmental laboratory is capable of producing accurate analytical data." [WAC 173-50-040] (Kammin, 2010)

Accuracy: The degree to which a measured value agrees with the true value of the measured property. USEPA recommends that this term not be used, and that the terms precision and bias be used to convey the information associated with the term accuracy. (USGS, 1998)

Analyte: An element, ion, compound, or chemical moiety (pH, alkalinity) which is to be determined. The definition can be expanded to include organisms, e.g., fecal coliform, Klebsiella. (Kammin, 2010)

Bias: The difference between the population mean and the true value. Bias usually describes a systematic difference reproducible over time, and is characteristic of both the measurement system, and the analyte(s) being measured. Bias is a commonly used data quality indicator (DQI). (Kammin, 2010; Ecology, 2004)

Blank: A synthetic sample, free of the analyte(s) of interest. For example, in water analysis, pure water is used for the blank. In chemical analysis, a blank is used to estimate the analytical response to all factors other than the analyte in the sample. In general, blanks are used to assess possible contamination or inadvertent introduction of analyte during various stages of the sampling and analytical process. (USGS, 1998)

Calibration: The process of establishing the relationship between the response of a measurement system and the concentration of the parameter being measured. (Ecology, 2004)

Check standard: A substance or reference material obtained from a source independent from the source of the calibration standard; used to assess bias for an analytical method. This is an obsolete term, and its use is highly discouraged. See Calibration Verification Standards, Lab Control Samples (LCS), Certified Reference Materials (CRM), and/or spiked blanks. These are all check standards, but should be referred to by their actual designator, e.g., CRM, LCS. (Kammin, 2010; Ecology, 2004)

Comparability: The degree to which different methods, data sets and/or decisions agree or can be represented as similar; a data quality indicator. (USEPA, 1997)

Completeness: The amount of valid data obtained from a project compared to the planned amount. Usually expressed as a percentage. A data quality indicator. (USEPA, 1997)

Continuing Calibration Verification Standard (CCV): A QC sample analyzed with samples to check for acceptable bias in the measurement system. The CCV is usually a midpoint calibration standard that is re-run at an established frequency during the course of an analytical run. (Kammin, 2010)

Control chart: A graphical representation of quality control results demonstrating the performance of an aspect of a measurement system. (Kammin, 2010; Ecology 2004)

Control limits: Statistical warning and action limits calculated based on control charts. Warning limits are generally set at +/- 2 standard deviations from the mean, action limits at +/- 3 standard deviations from the mean. (Kammin, 2010)

Data integrity: A qualitative DQI that evaluates the extent to which a data set contains data that is misrepresented, falsified, or deliberately misleading. (Kammin, 2010)

Data Quality Indicators (DQI): Commonly used measures of acceptability for environmental data. The principal DQIs are precision, bias, representativeness, comparability, completeness, sensitivity, and integrity. (USEPA, 2006)

Data Quality Objectives (DQO): Qualitative and quantitative statements derived from systematic planning processes that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions.
(USEPA, 2006)

Data set: A grouping of samples organized by date, time, analyte, etc. (Kammin, 2010)

Data validation: An analyte-specific and sample-specific process that extends the evaluation of data beyond data verification to determine the usability of a specific data set. It involves a detailed examination of the data package, using both professional judgment, and objective criteria, to determine whether the MQOs for precision, bias, and sensitivity have been met. It may also include an assessment of completeness, representativeness, comparability and integrity, as these criteria relate to the usability of the data set. Ecology considers four key criteria to determine if data validation has actually occurred. These are:
- Use of raw or instrument data for evaluation.
- Use of third-party assessors.
- Data set is complex.
- Use of EPA Functional Guidelines or equivalent for review.

Examples of data types commonly validated would be:
- Gas Chromatography (GC).
- Gas Chromatography-Mass Spectrometry (GC-MS).
- Inductively Coupled Plasma (ICP).

The end result of a formal validation process is a determination of usability that assigns qualifiers to indicate usability status for every measurement result. These qualifiers include:
- No qualifier – data are usable for intended purposes.
- J (or a J variant) – data are estimated, may be usable, may be biased high or low.
- REJ – data are rejected, cannot be used for intended purposes.
  (Kammin, 2010; Ecology, 2004).

Data verification: Examination of a data set for errors or omissions, and assessment of the Data Quality Indicators related to that data set for compliance with acceptance criteria (MQOs). Verification is a detailed quality review of a data set. (Ecology, 2004)

Detection limit (limit of detection)**:** The concentration or amount of an analyte which can be determined to a specified level of certainty to be greater than zero. (Ecology, 2004)

Duplicate samples: Two samples taken from and representative of the same population, and carried through and steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variability of all method activities including sampling and analysis. (USEPA, 1997)

Equipment blank: A blank used to obtain information on contamination introduced from decontaminated sampling equipment.

Field blank: A blank used to obtain information on contamination introduced during sample collection, storage, and transport. (Ecology, 2004)

Initial Calibration Verification Standard (ICV): A QC sample prepared independently of calibration standards and analyzed along with the samples to check for acceptable bias in the measurement system. The ICV is analyzed prior to the analysis of any samples. (Kammin, 2010)

Laboratory Control Sample (LCS): A sample of known composition prepared using contaminant-free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern. It is prepared and analyzed in the same batch of regular samples using the same sample preparation method, reagents, and analytical methods employed for regular samples. (USEPA, 1997)

Matrix spike: A QC sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias due to interference or matrix effects. (Ecology, 2004)

Measurement Quality Objectives (MQOs)**:** Performance or acceptance criteria for individual data quality indicators, usually including precision, bias, sensitivity, completeness, comparability, and representativeness. (USEPA, 2006)

Measurement result: A value obtained by performing the procedure described in a method. (Ecology, 2004)

Method: A formalized group of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, data analysis), systematically presented in the order in which they are to be executed. (EPA, 1997)

Method blank: A blank prepared to represent the sample matrix, prepared and analyzed with a batch of samples. A method blank will contain all reagents used in the preparation of a sample, and the same preparation process is used for the method blank and samples. (Ecology, 2004; Kammin, 2010)

Method Detection Limit (MDL): This definition for detection was first formally advanced in 40CFR 136, October 26, 1984 edition. MDL is defined there as the minimum concentration of an analyte that, in a given matrix and with a specific method, has a 99% probability of being identified, and reported to be greater than zero. (Federal Register, October 26, 1984)

Percent Relative Standard Deviation (%RSD): A statistic used to evaluate precision in environmental analysis. It is determined in the following manner:

$$\%RSD = (100 * s)/x$$

where s is the sample standard deviation and x is the mean of results from more than two replicate samples. (Kammin, 2010)

Parameter: A specified characteristic of a population or sample. Also, an analyte or grouping of analytes. Benzene and nitrate + nitrite are all "parameters." (Kammin, 2010; Ecology, 2004)

Population: The hypothetical set of all possible observations of the type being investigated. (Ecology, 2004)

Precision: The extent of random variability among replicate measurements of the same property; a data quality indicator. (USGS, 1998)

Quality assurance (CASQA): A set of activities designed to establish and document the reliability and usability of measurement data. (Kammin, 2010)

Quality Assurance Project Plan (QAPP): A document that describes the objectives of a project, and the processes and activities necessary to develop data that will support those objectives. (Kammin, 2010; Ecology, 2004)

Quality control (QC): The routine application of measurement and statistical procedures to assess the accuracy of measurement data. (Ecology, 2004)

Relative Percent Difference (RPD): RPD is commonly used to evaluate precision. The following formula is used:

$$[Abs(a-b)/((a + b)/2)] * 100$$

where "Abs()" is absolute value and a and b are results for the two replicate samples. RPD can be used only with 2 values. Percent Relative Standard Deviation is (%RSD) is used if there are results for more than 2 replicate samples (Ecology, 2004).

Replicate samples: Two or more samples taken from the environment at the same time and place, using the same protocols. Replicates are used to estimate the random variability of the material sampled. (USGS, 1998)

Representativeness: The degree to which a sample reflects the population from which it is taken; a data quality indicator. (USGS, 1998)

Sample (field): A portion of a population (environmental entity) that is measured and assumed to represent the entire population. (USGS, 1998)

Sample (statistical): A finite part or subset of a statistical population. (USEPA, 1997)

Sensitivity: In general, denotes the rate at which the analytical response (e.g., absorbance, volume, meter reading) varies with the concentration of the parameter being determined. In a specialized sense, it has the same meaning as the detection limit. (Ecology, 2004)

Spiked blank: A specified amount of reagent blank fortified with a known mass of the target analyte(s); usually used to assess the recovery efficiency of the method. (USEPA, 1997)

Spiked sample: A sample prepared by adding a known mass of target analyte(s) to a specified amount of matrix sample for which an independent estimate of target analyte(s) concentration is available. Spiked samples can be used to determine the effect of the matrix on a method's recovery efficiency. (USEPA, 1997)

Split sample: A discrete sample subdivided into portions, usually duplicates (Kammin, 2010)

Standard Operating Procedure (Matthes et al.): A document which describes in detail a reproducible and repeatable organized activity. (Kammin, 2010)

Surrogate: For environmental chemistry, a surrogate is a substance with properties similar to those of the target analyte(s). Surrogates are unlikely to be native to environmental samples. They are added to environmental samples for quality control purposes, to track extraction efficiency and/or measure analyte recovery. Deuterated organic compounds are examples of surrogates commonly used in organic compound analysis. (Kammin, 2010)

Systematic planning: A step-wise process which develops a clear description of the goals and objectives of a project, and produces decisions on the type, quantity, and quality of data that will be needed to meet those goals and objectives. The DQO process is a specialized type of systematic planning. (USEPA, 2006)

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