DEPARTMENT OF
ECOLOGY
State of Washington

Washington
State Department of
Agriculture

Copper in Surface Waters from Urban and Agricultural Watersheds

---

A Cooperative Study by the Washington State Departments of Ecology and Agriculture

October 2013

Ecology Publication No. 13-03-041

Agriculture Publication No. AGR PUB 102-392 (N/9/13)

Publication and Contact Information

This report is available on the Department of Ecology's website at
https://fortress.wa.gov/ecy/publications/SummaryPages/1303041.html

Data for this project are available at Ecology's Environmental Information Management (EIM) website www.ecy.wa.gov/eim/index.htm. Search Study ID DSAR0011.

The Activity Tracker Code for this study is 03-501.

For more information contact:

Publications Coordinator
Environmental Assessment Program
P.O. Box 47600, Olympia, WA 98504-7600
Phone: (360) 407-6764

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

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

Copper in Surface Waters from Urban and Agricultural Watersheds

A Cooperative Study by the Washington State Departments of Ecology and Agriculture

by

Paul D. Anderson and Evan Newell

Toxics Studies Unit
Environmental Assessment Program
Washington State Department of Ecology
Olympia, Washington 98504-7710

Water Resource Inventory Area (WRIA) and 8-digit Hydrologic Unit Code (HUC) numbers for the study area:

WRIAs
- 3 Lower Skagit-Samish
- 9 Green-Duwamish
- 37 Lower Yakima
- 45 Wenatchee
- 46 Entiat

HUC numbers
- 17020010
- 17020011
- 17030003
- 17110002
- 17110007
- 17110019

This page is purposely left blank

Table of Contents

Page

List of Figures

List of Tables

Abstract

A 2011 study by the Washington State Department of Ecology on sources of toxic chemicals identified urban lawn and garden use of copper as potentially the largest source of copper entering the Puget Sound basin. To help evaluate this conclusion, copper sampling of fresh surface waters was conducted in 2012 as part of an ongoing monitoring program, *Pesticides in Surface Waters in Salmonid-Bearing Streams.* Both urban and agricultural streams were sampled.

In addition to evaluating copper levels in surface waters, a subset of four locations was selected to make a comparison between the Washington State water quality criteria and the Biotic Ligand Model (BLM) recommended criteria. The BLM uses ten parameters to assess potential copper toxicity.

In general, copper concentrations were below Washington State criteria. One sample from Brown Slough was above the marine water quality criteria for copper. Copper concentrations in western Washington from urban and agricultural sites were similar. Overall, concentrations in the eastern Washington agricultural sites were lower than in all of the western Washington agricultural sites.

A Wilcoxon Rank-Sum test showed that there is a statistically significant difference between the State criteria and the BLM criteria. The BLM acute and chronic criteria were significantly lower than the State criteria at Marion Drain and Longfellow Creek. At the Samish and Wenatchee Rivers, the BLM acute and chronic criteria were significantly higher than the State criteria.

Acknowledgements

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

- George Tuttle and Kelly McClain, Washington State Department of Agriculture, for field assistance, document review, and technical assistance.
- Elizabeth Sanchey, Program Manager for the Yakama Nation Environmental Management Program, for technical assistance.
- Mike Jurgens for permission to access the Mission Creek site.
- Washington State Department of Ecology staff:
    - For field assistance: Michael Friese, Matt Bischof, Casey Deligeannis, Jenna Durkee, Brandee Era-Miller, Joye Redfield-Wilder, Suzanne Saunders, Keith Seiders, and Eiko Urmos-Berry.
    - Manchester Environmental staff for sample processing, sample analysis, review of results, and technical assistance: Bob Carrell, Karin Feddersen, Kamilee Ginder, Dickey Huntamer, Stuart Magoon, Dean Momohara, Nancy Rosenbower, John Weakland, Leon Weiks, and Jeff Westerlund.
    - Debby Sargeant and Dale Norton for review.
    - David Osterberg for peer review.

Introduction

A report completed by the Washington State Department of Ecology (Ecology), *Control of Toxic Chemicals in Puget Sound: Assessment of Selected Toxic Chemicals in the Puget Sound Basin, 2007-2011* (Norton et al., 2011), identified urban lawn and garden use of copper as potentially one of the largest sources of copper in the Puget Sound basin. This conclusion was based on estimates of copper use from per capita use rates reported by the Oregon Department of Agriculture (ODA) and the California Department of Pesticide Regulation (CDPR) (Ecology, 2011). While the data sets from Oregon and California provided a range of estimates, the report recommended collecting additional data specific to Washington.

This report provides additional data on copper in salmon-bearing streams in support of ongoing efforts to estimate copper use in Washington. The Washington State Department of Agriculture (WSDA) is also conducting a pesticide use survey in some of the areas that were sampled as part of this project.

To provide additional data on copper use, Ecology capitalized on existing efforts to monitor pesticides in salmon-bearing streams. The *Pesticides in Surface Waters in Salmonid-Bearing Streams* program is an on-going sampling effort by the WSDA and Ecology that has been in existence since 2003. The study assesses pesticide presence in salmon-bearing streams during the typical pesticide-use season. Sampling sites are monitored weekly from March through September and are located in urban areas of Seattle and diverse agricultural areas of western and eastern Washington.

Copper was added to the list of analytes for this project, but funding constraints limited copper sampling to every other week. All copper results were compared to the Washington State water quality criteria (WAC 173-201A, 2006). These criteria are comprised of acute and chronic criteria that are calculated based on the hardness of the water being evaluated.

In recent years, the U.S. Environmental Protection Agency (EPA) developed a model for copper that uses multiple parameters to assess toxicity, availability, and calculate recommended acute and chronic water quality criteria. This model is called the Biotic Ligand Model (BLM).

To run the BLM, ten additional parameters are needed: dissolved organic carbon, calcium, magnesium, sodium, potassium, sulfate, chloride, alkalinity, pH, and temperature. Due to budget constraints, only a subset of sites from western and eastern Washington was sampled once per month for seven months. All copper results from the subset of sites were compared to the BLM water quality criteria.

Study Design

The main goal of this study was to determine if there are elevated copper concentrations in urban and agricultural areas that can be related to pesticide use. The *Pesticides in Surface Waters of Salmonid-Bearing Streams* program is an existing study that has an established sampling regime in both urban and agricultural areas. The program samples once per week from early March through early September at 15 sites. Pesticides are the main focus of the project, but conventional parameters are also measured because they can affect the toxicity of pesticides and also impact salmon and their prey base.

This study fit well with the study design of the *Pesticides in Surface Waters of Salmonid-Bearing Streams* program, so the two studies were combined for a single sampling season. Detailed information about the study design of this project can be found in the Quality Assurance (QA) Project Plan addendum (Anderson, 2012).

Further information on the *Pesticides in Surface Waters of Salmonid-Bearing Streams* program can be found in the original QA Project Plan (Johnson and Cowles, 2003) and subsequent addendums (Burke and Anderson, 2006; Dugger et al., 2007; Anderson and Sargeant, 2009; Anderson, 2011).

Sampling Locations

Thirteen of the 15 sites were sampled based on location and available resources. Location was important because the primary intent of this project was to determine if elevated levels of copper are present in urban and agricultural streams in the Puget Sound basin. Other locations were sampled to provide additional data on copper in agricultural areas and to have a spatially diverse dataset to compare the Washington State water quality criteria to the BLM.

Western Washington sampling locations were selected if they drained directly to Puget Sound. Two of the seven western Washington sites (Thornton Creek and upstream Big Ditch) did not fit this criterion. Thornton Creek drains to Lake Washington, and upstream Big Ditch was not used because it is located upstream of another location. Sampling this site would not provide any added value to the study. All of the eastern Washington sites were sampled.

The five sampling sites selected in western Washington were: Longfellow Creek, Samish River, Brown Slough, downstream Big Ditch, and Indian Slough. The remaining sites in eastern Washington were: Wenatchee River, Peshastin Creek, Brender Creek, Mission Creek, Entiat River, Marion Drain, Sulphur Creek Wasteway, and Spring Creek. A map showing the locations of the sampling sites is presented in Figure 1. In addition, Table 1 provides information about site classification and location. Further detailed information on sampling locations and descriptions are provided in Appendix A, Table A-1.

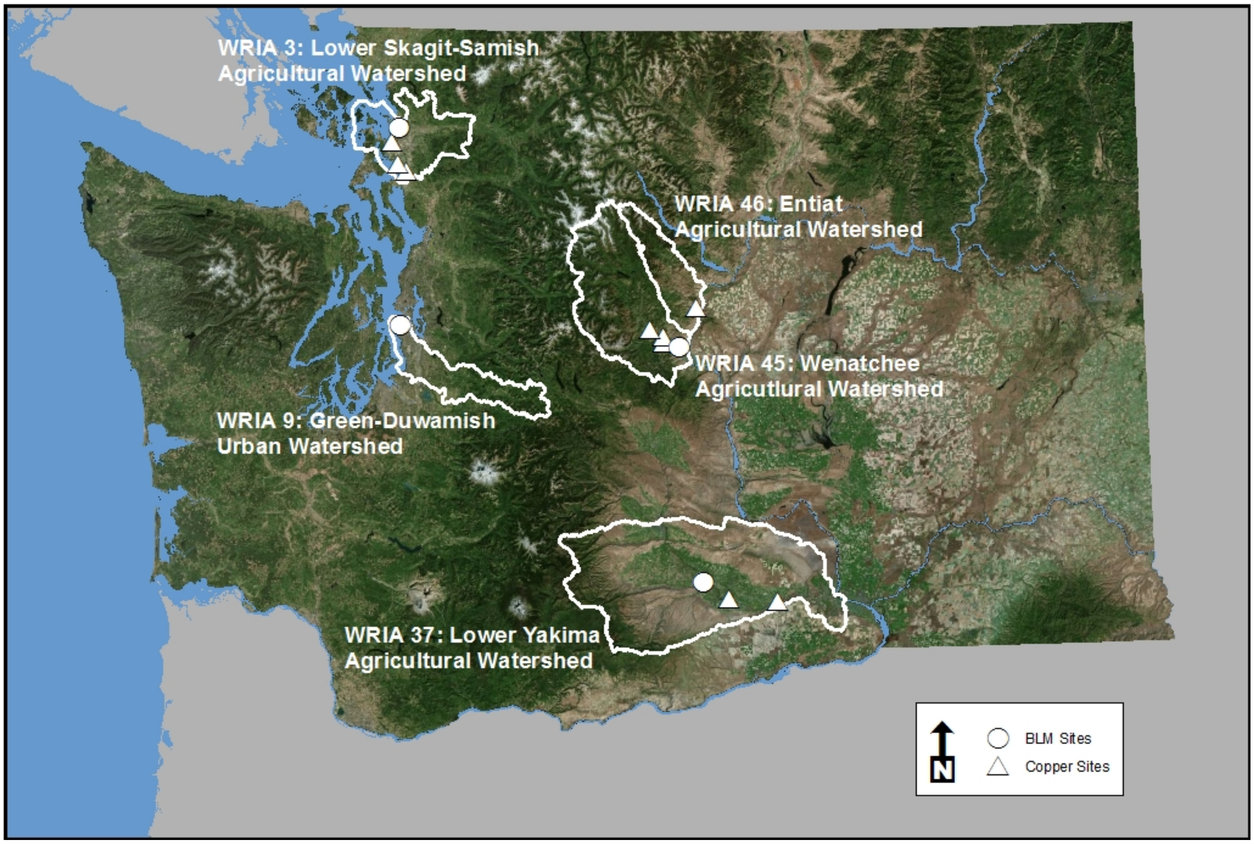

Figure 1. Copper and Biotic Ligand Model (BLM) sampling locations.

Table 1. Site name, geographic classification, watershed, land use, and BLM use designation.

Site Name	Geographic Class	Watershed	Land Use Class	BLM Site
Longfellow Creek	West	Green-Duwamish	Urban	Yes
Samish River	West	Skagit-Samish	Agricultural	Yes
Brown Slough	West	Skagit-Samish	Agricultural	No
Big Ditch (downstream)	West	Skagit-Samish	Agricultural	No
Indian Slough	West	Skagit-Samish	Agricultural	No
Wenatchee River	East	Wenatchee	Agricultural	Yes
Peshastin Creek	East	Wenatchee	Agricultural	No
Brender Creek	East	Wenatchee	Agricultural	No
Mission Creek	East	Wenatchee	Agricultural	No
Entiat River	East	Entiat	Agricultural	No
Marion Drain	East	Lower Yakima	Agricultural	Yes
Sulphur Creek Wasteway	East	Lower Yakima	Agricultural	No
Spring Creek	East	Lower Yakima	Agricultural	No

Parameters

All of the sites were sampled for dissolved copper and hardness. In addition to dissolved copper, total recoverable copper was included at the five western Washington sites. Total recoverable copper was sampled in western Washington for use in loading calculations.

In order to compare the BLM water quality criteria to the Washington State water quality criteria, 10 parameters were needed. Two of these 10 (pH and temperature) were collected as part of the on-going project. The remaining eight (dissolved organic carbon, calcium, sodium, magnesium, potassium, sulfate, chloride, and alkalinity) were added for this study. Due to the expense of the additional parameters only four sites were able to be sampled once per month for the seven months of the *Pesticides in Surface Waters of Salmonid-Bearing Streams* program sampling season.

Sample Timing

Samples were collected every other week during the sampling season which began the second week of March. There were a total of 14 sampling events over the 27-week sampling season.

Methods

Field Procedures

Collection of water samples for metals followed Ecology's Standard Operating Procedure (SOP) EAP029 *Collection and Field Processing of Metals Samples* (Ward, 2010). Dissolved metal samples were filtered in the field within 15 minutes of collection using pre-cleaned filters provided by the Manchester Environmental Laboratory (MEL).

Non-metal water samples were collected by hand as simple grabs from mid-channel following Ecology's SOP EAP015 Manually Obtaining Surface Water Samples (Joy, 2006).

Sample and transfer containers were delivered pre-cleaned by the manufacturer to EPA specifications (EPA, 1990). After collection, all samples were labeled and preserved according to each individual analysis method as described in Addendum 5 of the QA Project Plan (Anderson, 2012).

Temperature and pH were measured in the field using a Series 5 Hydrolab® MiniSonde® multiprobe following Ecology's SOP EAP033 Hydrolab® DataSonde® and MiniSonde® Multiprobes (Swanson, 2007).

Discharge was measured in the field using a Marsh-McBirney Model 2000 flowmeter and top-setting wading rod, as described in Ecology's SOP EAP056 (Shedd, 2011). Due to the size of the Samish River, flow measurements cannot always be obtained. When flow measurements were unavailable, rating curves based on staff gauge readings and upstream flow measurements from the U.S. Geological Survey (USGS) were used. The discharge volumes associated with the times that flow measurements were unavailable are considered estimates.

Laboratory Procedures

Ecology's MEL analyzed all samples collected for this study according to current laboratory SOPs. Laboratory methods are presented in Table 2.

Table 2. Laboratory reporting limits and analytical methods.

Analysis	Reporting Limit	Analytical Method
Copper*	0.1 ug/L	ICP/MS EPA 200.8
Calcium, Magnesium, Sodium	50 ug/L	ICP/MS EPA 200.9
Potassium	500 ug/L	ICP/MS EPA 200.10
Hardness	0.3 mg/L	SM2340B
DOC	1 mg/L	SM5310B
Sulfate	0.5 mg/L	EPA 300.0; SM4110C
Chloride	0.1 mg/L	EPA 300.0; SM4110C
Alkalinity	5 mg/L	EPA 310.2; SM2320B

*Used for both total recoverable and dissolved fractions.
DOC: dissolved organic carbon
EPA: Environmental Protection Agency
ICP/MS: inductively coupled plasma/mass spectrometry
SM: standard method

Data Quality

Performance of laboratory analyses is governed by quality assurance and quality control (QA/QC) protocols. The QA/QC protocols employ application of blanks (field and laboratory), laboratory control samples (LCS), and laboratory duplicates. Laboratory blanks, LCSs, and duplicates are analyzed as the laboratory component of QA/QC. Field blanks and filter blanks integrate field and laboratory components. Case narratives describing the quality of the data are available upon request. Quality assurance data can be found in Appendix B.

Laboratory Data Quality

Laboratory control samples, duplicates, matrix spikes, and matrix spike duplicates (MS/MSDs) were assessed using measurement quality objectives (MQOs) established in the MEL Quality Assurance Manual (MEL, 2012). MQOs for the QA/QC analyses used in this project are shown in Appendix B, Table B-1. All laboratory QA/QC samples met MQOs with the following exceptions:

- One sample was analyzed at a dilution due to matrix interference. The reporting limit for this sample was raised accordingly.
- Matrix spike and matrix spike duplicate recoveries for two hardness samples were outside acceptance levels due to matrix interference. The source samples were qualified as estimates.
- Matrix spike and matrix spike duplicate recoveries for hardness, calcium, and magnesium in one sample were outside acceptance levels. The standard spiking level was insufficient for the measured concentration in the source sample. No corrective action was taken because no evaluation was made.

The laboratory received all samples within the proper temperature range of 0 – 4 °C. All analyses were performed within holding times. No analytically significant levels of analytes were detected in laboratory method blanks. All internal standard recoveries were within acceptance limits.

Field Data Quality

Blanks

For the copper analysis, transfer and filter blanks were analyzed to evaluate the potential for contamination during sample handling and processing procedures in the field. Transfer and filter blanks were prepared using blank water from MEL. To prepare the blanks, 1 liter of blank water was split in half. For transfer blanks, half of the blank water was transferred directly into a sample bottle. Filter blanks were prepared in a similar manner; the difference was that the blank water was passed through a 0.45 um filter before being transferred to a sample bottle. Transfer blanks were analyzed for total recoverable copper, and filter blanks were analyzed for dissolved copper. Transfer and filter blanks were scheduled on a quarterly basis and were collected at the beginning of each quarter.

Blank Contamination

Results from transfer and filter blanks showed low level contamination from both total recoverable copper and dissolved copper (Appendix B, Table B-2). Enough time was left after receiving the results of the third quarter blanks to add more transfer and filter blanks to investigate the source of the contamination. It was suspected that the source of the contamination was the glass 1-liter bottles that MEL used to supply the blank water. Normally blank water for metals is provided in Teflon bottles. It is unclear why the blank water was supplied in the 1-liter glass bottles.

To test if the glass bottles were the source of the blank contamination, new blank water was requested in 500 mL Teflon bottles. This new blank water was used to do a side-by-side comparison with the blank water from the glass 1-liter bottles. The side-by-side comparison consisted of preparing two sets of transfer and filter blanks. One set was done with blank water from the Teflon bottles and the other was done with blank water from 1-liter glass bottles. Both sets were prepared in a lab at Ecology's Environmental Assessment Program Operations Center.

The blank prepared using water from the Teflon bottles showed no detections while the blank prepared using the 1-liter glass showed detections in total recoverable and dissolved copper. While this shows that the 1-liter glass bottles most likely were the source of the contamination, not enough samples were able to be analyzed to be sure. There also is not enough data to adjust for the blank contamination.

Corrective Action

The five times rule was applied to all results from the date and area associated with the contaminated blank. For the data associated with the contaminated blanks to be valid, the five times rule requires that a result has to be at least five times greater than the reported blank result. All results associated with the blank that were less than five times the reported blank result were qualified as a UJ[1]. In addition, all associated results that were five times greater than the reported blank were qualified as an estimate (J).

Due to the blank contamination, an additional blank per month was added for the remaining two months of the study. These additional blanks were performed on both the west and east sides of the state. Transfer and filter blanks were prepared using blank water from MEL in Teflon bottles.

Blank results for the month of August did not show any blank contamination. However, the blanks for the month of September showed contamination. The blank results from Mission

---

[1] UJ – The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.

Creek appear to be the result of sample switch that occurred in the field or at MEL. The sample result for Mission Creek was reported as a non-detect. This non-detect did not fit the detection pattern of the site over the sample period. The blank result is similar to results that were seen over the sampling period. However, no direct evidence is available to determine if an error did occur. Therefore, the results associated with the Mission Creek blank were qualified according to the five times rule discussed earlier.

Field Measurement Data Quality

Hydrolabs were calibrated at the beginning of the field day according to the manufacturers' specifications, using Ecology's SOP EAP033 (Swanson, 2007). Flow meters were zeroed at the beginning of each field day following manufacturer instructions.

Hydrolabs were post checked at the end of the field day using known standards. Post checks met MQOs described in Addendum 3 of the QA Project Plan for the *Pesticides in Surface Waters of Salmonid-Bearing Streams* program (Anderson and Sargeant, 2009).

This page is purposely left blank

Results

Results for this 2012 study are summarized by site in the following sections. All results are available through Ecology's EIM system, www.ecy.wa.gov/eim/.

Longfellow Creek

Copper and Hardness

Dissolved and total recoverable copper as well as hardness concentrations for Longfellow Creek are shown in Table 3. Dissolved copper concentrations ranged from 0.83 to 2.55 ug/L. Concentrations of total recoverable copper ranged from 1.42 to 3.76 ug/L. Hardness ranged from 92.6 to 140 mg/L. The highest concentrations for both dissolved and total recoverable copper occurred in late March, early May, and early June. These concentrations of copper coincided with the lowest hardness concentrations.

Table 3. Dissolved and total recoverable copper (ug/L) and hardness (mg/L) concentrations for Longfellow Creek.

Date	Dissolved Copper (ug/L)	Total Recoverable Copper (ug/L)	Percent Dissolved	Hardness (mg/L)
3/9/2012	1.20	1.87 J	64	139
3/23/2012	2.12	2.59 J	82	124
4/6/2012	1.96 J	2.24	88	130
4/17/2012	1.51 J	1.83	83	137
5/3/2012	2.55 J	3.76	68	92.6
5/15/2012	1.23 J	1.62	76	140
6/1/2012	2.54 J	2.71	94	105
6/15/2012	1.06 J	1.42	75	140
6/25/2012	1.60 J	1.90	84	123
7/13/2012	0.96 J	1.56 J	62	138
7/23/2012	1.15 J	1.42 J	81	130
8/10/2012	REJ	REJ	-	133
8/20/2012	0.95	1.53	62	135
9/4/2012	0.83	2.02 UJ	-	132

J: The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

UJ: The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.

REJ: The sample results are rejected.

In all of the comparable sample pairs, the dissolved fraction makes up the majority of the concentration of copper (Table 3). Most of the dissolved copper and several of the total recoverable copper results were qualified as estimates (J) due to blank contamination. The total recoverable result for the final sample taken on 9/4/2012 had to be qualified as a non-detect (UJ) due to blank contamination. This non-detect qualified sample cannot be used for comparison.

Conventionals

Table 4 shows all of the data for the conventional parameters that were collected from Longfellow Creek. All of the parameters, except temperature, had little variation over the seven months of sampling. Temperature showed a seasonal pattern during the sampling period (March – September). Water temperature increased from the start of sampling in the spring, peaked in July and then began cooling with the approach of fall (Table 4). One other notable difference in the data occurred on 6/1/2012. On this sampling day all parameters except pH and temperature had results that were lower than the rest of the sampling period (Table 4).

Table 4. Conventional parameters for Longfellow Creek.

Date	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Alk (mg/L)	DOC (mg/L)	pH	Temp. (°C)
3/9/2012	25.6	17.4	11.7	2.48	23.7	11.6	118	2.9	8.2	7.40
4/6/2012	24.9	14.9	9.89	2.43	20.4	9.20	118	3.6	7.7	10.8
5/15/2012	24.8	18.1	10.7	2.40	23.3	10.2	125	2.6	8.2	14.9
6/1/2012	20.4	13.9	8.48	2.27	16.8	8.08	103	4.1	7.5	15.4
7/13/2012	22.1	17.0	10.2	2.43	24.7	9.42	123	2.1	7.7	16.7
8/10/2012	22.8	18.5	10.3	2.46	26.1	9.15	121	2.0	7.8	15.9
9/4/2012	22.3	18.9	10.3	2.62	26.3	8.96	122	1.9	7.9	14.5

Alk: Alkalinity
Ca: Calcium
DOC: Dissolved Organic Carbon
K: Potassium
Mg: Magnesium
Na: Sodium

Samish River

Copper and Hardness

Concentrations of dissolved and total copper as well as hardness for the Samish River are shown in Table 5. Dissolved copper concentrations ranged from 0.63 to 1.54 ug/L. Total recoverable copper ranged from 0.96 to 4.61 ug/L. Hardness ranged from 26.2 to 54.8 mg/L. The highest concentrations of dissolved and total recoverable copper occurred from March through early May and in late June (Table 5). These concentrations of copper coincided with the lowest hardness samples.

Between March and early May most of the copper in each sample is made up of total recoverable copper. After early May most of the copper in each sample is from the dissolved fraction. Three of the samples could not be compared due to non-detect qualifiers.

Table 5. Dissolved and total recoverable copper (ug/L) and hardness (mg/L) concentrations for the Samish River.

Date	Dissolved Copper (ug/L)	Total Recoverable Copper (ug/L)	Percent Dissolved	Hardness (mg/L)
3/9/2012	1.10	2.64 J	42	29.8
3/23/2012	0.93	2.17 J	43	31.5
4/6/2012	1.09 J	2.57	42	29.5
4/17/2012	1.54 J	4.61	33	27.0
5/4/2012	1.32 J	3.22	41	26.2
5/15/2012	0.90 J	1.76	51	34.3
6/1/2012	1.17 J	1.59	74	34.8
6/15/2012	0.87 J	1.19	73	39.5
6/25/2012	1.17 J	2.15	54	28.7
7/13/2012	0.86 UJ	1.49 J	-	40.1
7/23/2012	0.77 UJ	1.22 J	-	41.4
8/10/2012	0.68	0.96	71	50.4
8/20/2012	0.63	0.96	66	52.8
9/4/2012	0.63	0.96 UJ	-	54.8

J: The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
UJ: The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.

Conventionals

All of the data for the parameters used in the BLM that were collected from the Samish River are shown in Table 6. All of the parameters except DOC, pH, and temperature showed an increasing pattern after the first sample collection in March. From the first sample collection to the second there was a decrease (Table 6). Dissolved organic carbon and pH showed little variation over the sampling period. Temperature data show a seasonal pattern with cooler temperatures starting in the spring and maximum temperatures in July (Table 6).

Table 6. Conventional parameters for the Samish River.

Date	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Alk (mg/L)	DOC (mg/L)	pH	Temp. (°C)
3/9/2012	7.79	2.93	3.89	1.01	4.05	3.88	22.4	2.6	7.7	6.4
4/6/2012	7.33	2.72	3.34	0.85	3.79	3.34	24.7	2.8	7.4	7.1
5/15/2012	8.95	3.40	3.71	0.74	3.86	3.22	34.6	2.4	7.2	13.5
6/1/2012	9.56	3.48	3.70	0.80	3.96	3.27	34.4	2.4	7.3	12.4
7/13/2012	9.11	3.22	3.76	0.83	4.00	3.45	38.6	2.5	7.6	15.9
8/10/2012	12.4	4.95	4.86	1.12	5.19	4.15	51.4	2.2	7.7	14.8
9/4/2012	13.1	5.42	4.94	1.24	5.80	6.46	56.6	1.6	7.9	15.0

Alk: Alkalinity
Ca: Calcium
DOC: Dissolved Organic Carbon
K: Potassium
Mg: Magnesium
Na: Sodium

Brown Slough

Copper and Hardness

Brown Slough concentrations of dissolved and total recoverable copper as well as hardness are shown in Table 7. Dissolved copper ranged from 0.22 to 3.82 ug/L and total recoverable copper ranged from 0.78 to 3.90 ug/L. Hardness ranged from 226 to 2510 mg/L. The highest concentrations of copper were found in early May and early September. An outlier hardness value from the last sample event coincided with the highest detection of dissolved and total copper (Table 7).

Five out of the nine comparable copper sample pairs had dissolved copper concentrations greater than 50%. There was no discernible pattern for when the dissolved copper concentration was higher or lower than total recoverable concentration.

Table 7. Dissolved and total recoverable copper (ug/L) and hardness (mg/L) concentrations for Brown Slough.

Date	Dissolved Copper (ug/L)	Total Recoverable Copper (ug/L)	Percent Dissolved	Hardness (mg/L)
3/9/2012	0.70	1.82 J	38	902
3/23/2012	0.89	1.89 J	47	817
4/6/2012	0.64 J	1.71	37	940
4/17/2012	1.05 J	1.76	60	903
5/4/2012	0.52 UJ	3.37	15	474
5/15/2012	0.50 UJ	1.49	34	730
6/1/2012	1.06 J	1.10	96	660
6/15/2012	0.94 J	1.23	76	716
6/25/2012	1.00 U	1.15	-	280
7/13/2012	0.67 UJ	1.05 J	64	402
7/23/2012	0.53 UJ	0.78 J	68	402
8/10/2012	0.22	1.43	15	650
8/20/2012	0.76	1.43	53	226
9/4/2012	3.82	3.90 J	98	2510

J: The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
UJ: The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.

Indian Slough

Copper and Hardness

Table 8 shows the dissolved and total recoverable copper concentrations as well as the hardness results for Indian Slough. Dissolved copper ranged from 0.58 to 3.02 ug/L and total recoverable copper ranged from 0.64 to 4.43 ug/L. Hardness ranged from 70.7 to 387 mg/L. The highest dissolved and total recoverable copper concentrations occurred from early April through the beginning of May. These copper concentrations coincided with the lowest hardness sample results (Table 8). With the exception of the sample from late June, copper concentrations after mid-May were several times lower in the summer than in the spring.

In all of the comparable sample pairs, the dissolved concentration makes up the majority of the copper in each sample (Table 8). Several copper sample pairs were not comparable due to non-detect qualifiers.

Table 8. Dissolved and total recoverable copper (ug/L) and hardness (mg/L) concentrations for Indian Slough.

Date	Dissolved Copper (ug/L)	Total Recoverable Copper (ug/L)	Percent Dissolved	Hardness (mg/L)
3/9/2012	1.39	2.73 J	51	117
3/23/2012	2.01	3.20 J	63	102
4/6/2012	2.61 J	4.34	60	87.4
4/17/2012	2.35 J	4.42	53	70.7
5/4/2012	3.02 J	4.43	68	97.9
5/15/2012	0.83 J	1.1	75	112
6/1/2012	0.89 J	0.97	92	259
6/15/2012	0.62 J	0.73	85	176
6/25/2012	2.31 J	3.26	71	124
7/13/2012	0.68 UJ	0.86 J	-	130
7/23/2012	0.48 UJ	0.64 J	-	182
8/10/2012	0.61	0.90	68	387
8/20/2012	0.58	0.80	73	151
9/4/2012	0.83	0.71 UJ	-	191

J: The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
UJ: The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.

Big Ditch

Copper and Hardness

Dissolved and total recoverable copper concentrations and hardness values for downstream Big Ditch are shown in Table 9. Dissolved copper ranged from 0.60 to 5.57 ug/L, and total recoverable copper ranged from 0.96 to 14.8 ug/L. Hardness ranged from 19.5 to 189 mg/L. Highest concentrations of copper were seen from March through early May. The peak copper concentration occurred in early May and was many times higher than any of the other sample results (Table 9).

From late June until September the dissolved concentration of the comparable sample pairs made up the majority of the copper in the samples. The majority fraction (i.e., dissolved or particulate) varied for all of the samples before the end of June (Table 9). One copper sample pair was not comparable due to a non-detect qualifier.

On 6/1/2012 the dissolved copper concentration was slightly higher than the total recoverable concentration. This could have occurred because of the accuracy of the method. Looking at the results it is clear that most if not all of the sample is in the dissolved fraction. Results from the dissolved analysis show the entire amount. This is not true for the total recoverable analysis. As the name states, the analysis only provides a result for the total amount of copper that is recoverable. This means that there may have been more copper in the sample but the analysis was not able to detect it.

Table 9. Dissolved and total recoverable copper (ug/L) and hardness (mg/L) concentrations for downstream Big Ditch.

Date	Dissolved Copper (ug/L)	Total Recoverable Copper (ug/L)	Percent Dissolved	Hardness (mg/L)
3/9/2012	2.44	6.01 J	41	187
3/23/2012	2.82	5.29 J	53	184
4/6/2012	2.74 J	6.08	45	188
4/17/2012	2.69 J	5.09	53	126
5/4/2012	5.57 J	14.8	38	110
5/15/2012	1.85 J	2.66	70	189
6/1/2012	2.26 J	2.20	103	166
6/15/2012	0.74 J	1.70	44	55.2
6/25/2012	2.32 J	3.70	63	140
7/13/2012	1.30 J	1.79 J	73	95.0
7/23/2012	1.10 J	1.41 J	78	63.7
8/10/2012	0.60	1.10	55	19.5
8/20/2012	0.63	0.96	66	23.6
9/4/2012	0.73	0.8 UJ	-	38.8

J: The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

UJ: The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.

Wenatchee River

Dissolved Copper and Hardness

Dissolved copper and hardness results for the Wenatchee River are shown in Table 10. Dissolved copper concentrations ranged from 0.33 to 0.55 ug/L. Hardness results ranged from 10.7 to 44.0 mg/L. The highest dissolved copper concentrations were in April. Hardness declined from April through early July and then increased from late July to the last sample in September (Table 10).

Table 10. Dissolved copper (ug/L) and hardness (mg/L) concentrations for the Wenatchee River.

Date	Dissolved Copper (ug/L)	Hardness (mg/L)
3/5/2012	0.39	35.4
3/21/2012	0.41	38.1
4/4/2012	0.55	44.0
4/17/2012	0.48	34.6
5/1/2012	0.41	20.5
5/15/2012	0.42	18.3
5/30/2012	0.42	15.1
6/11/2012	0.37	16.8
6/26/2012	0.33	13.3
7/10/2012	0.36	10.7
7/25/2012	0.33	15.3
8/6/2012	0.38	16.0
8/21/2012	0.35	20.1
9/5/2012	0.34 UJ	29.2

UJ: The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.

Conventionals

Data for the parameters used in the BLM that were collected from the Wenatchee River are presented in Table 11. Dissolved organic carbon showed little variation over the sampling period. All of the parameters, except pH and temperature, show an increase from March to April followed by a deceasing pattern through July. After July the data show an increasing pattern. Temperature data show a seasonal pattern with cooler temperatures starting in the spring and maximum temperatures in August (Table 11).

Table 11. Conventional parameters for the Wenatchee River.

Date	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Alk (mg/L)	DOC (mg/L)	pH	Temp. (°C)
3/5/2012	7.32	3.87	3.15	1.12	2.72	3.66	30.8	1.3	8.8	6.2
4/4/2012	9.38	4.95	3.81	1.30	3.13	4.49	44.5	1.9	8.3	5.7
5/15/2012	3.80	2.20	1.33	0.90	1.58	0.68	14.1	1.7	7.4	9.0
5/30/2012	3.81	1.72	1.27	0.83	1.62	0.65	13.3	1.5	7.7	8.5
7/10/2012	2.56	1.14	0.85	0.67	1.35	0.30	8.0	1.2	7.5	13.1
8/6/2012	3.88	1.70	1.25	0.88	1.96	0.78	13.7	1.1	8.0	19.9
9/5/2012	6.39	3.42	2.28	1.12	3.03	1.6	32.2	1.2	9.0	18.5

Alk: Alkalinity
Ca: Calcium
DOC: Dissolved Organic Carbon
K: Potassium
Mg: Magnesium
Na: Sodium

Peshastin Creek

Dissolved Copper and Hardness

Table 12 shows the dissolved copper and hardness results for Peshastin Creek. Dissolved copper concentrations ranged from 0.28 to 0.55 ug/L. Hardness results ranged from 34.4 to 101 mg/L. Hardness results showed a similar pattern to the Wenatchee River with a decrease over the sampling period until late July when concentrations increased. The highest dissolved copper concentrations in Peshastin Creek were in April (Table 12).

Table 12. Dissolved copper (ug/L) and hardness (mg/L) concentrations for Peshastin Creek.

Date	Dissolved Copper (ug/L)	Hardness (mg/L)
3/5/2012	0.41	95.6
3/21/2012	0.39	101 J
4/4/2012	0.62	101
4/17/2012	0.55	80.8
5/1/2012	0.49	60.9
5/15/2012	0.39	47.2
5/30/2012	0.32	46.6
6/11/2012	0.32	46.9
6/26/2012	0.32	41.1
7/10/2012	0.33	34.4
7/25/2012	0.28	46.3
8/6/2012	0.40	50.9
8/21/2012	0.32	51.4
9/5/2012	0.34 UJ	57.1

J: The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
UJ: The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.

Brender Creek

Dissolved Copper and Hardness

Dissolved copper and hardness results for Brender Creek are shown in Table 13. Dissolved copper ranged from 0.47 to 1.39 ug/L. Hardness results ranged from 65.4 to 189 mg/L. Peak concentrations of dissolved copper were in April and August with the highest result occurring in late August. The highest hardness values occurred in March and April.

Table 13. Dissolved copper (ug/L) and hardness (mg/L) concentrations for Brender Creek.

Date	Dissolved Copper (ug/L)	Hardness (mg/L)
3/5/2012	0.64	189
3/21/2012	0.56	187
4/4/2012	1.25	174
4/17/2012	0.75	171
5/1/2012	0.59	85.1
5/15/2012	0.57	86.3
5/30/2012	0.73	76.0
6/11/2012	0.47	68.9
6/26/2012	0.52	65.4
7/10/2012	0.62	67.7
7/25/2012	0.54	85.5
8/6/2012	0.85	78.2
8/21/2012	1.39	78.9
9/5/2012	0.74 UJ	82.4

UJ: The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.

Mission Creek

Dissolved Copper and Hardness

Mission Creek results for dissolved copper and hardness are presented in Table 14. Concentrations of dissolved copper ranged from 0.40 to 0.73 ug/L. Hardness results ranged from 74.1 to 123 mg/L. Highest hardness results occurred in March. Peak concentrations of dissolved copper were in April (Table 14).

Table 14. Dissolved copper (ug/L) and hardness (mg/L) concentrations for Mission Creek.

Date	Dissolved Copper (ug/L)	Hardness (mg/L)
3/5/2012	0.55	123
3/21/2012	0.56	120
4/4/2012	0.7	114
4/17/2012	0.73	98.9
5/1/2012	0.58	82.8
5/15/2012	0.54	74.1
5/30/2012	0.48	81.4
6/11/2012	0.46	83.4
6/26/2012	0.40	89.3
7/10/2012	0.46	95.7
7/25/2012	0.47	100
8/6/2012	0.45	101
8/21/2012	0.43	108
9/5/2012	0.10 UJ	113

U: The analyte was not detected at or above the reported sample quantitation limit.

Entiat River

Dissolved Copper and Hardness

Table 15 presents dissolved copper and hardness results for the Entiat River. Dissolved copper concentrations ranged from 0.15 to 0.26 ug/L. Hardness values ranged from 12.0 to 49.8 mg/L. The highest concentrations of copper were in April (Table 15). Overall, the copper concentrations were similar over the sampling period. Compared to other sites from this study, hardness values were low.

Table 15. Dissolved copper (ug/L) and hardness (mg/L) concentrations for the Entiat River.

Date	Dissolved Copper (ug/L)	Hardness (mg/L)
3/5/2012	0.23	48.3
3/21/2012	0.19	49.8
4/4/2012	0.26	52.2
4/17/2012	0.25	44.1
5/1/2012	0.24	22.4
5/15/2012	0.23	15.8
5/30/2012	0.21	15.0
6/11/2012	0.15	16.0
6/26/2012	0.16	13.1
7/10/2012	0.17	12.0
7/25/2012	0.17	18.8
8/6/2012	0.18	20.3
8/21/2012	0.19	25.2
9/5/2012	0.20 UJ	32.9

UJ: The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.

Marion Drain

Dissolved Copper and Hardness

Dissolved copper and hardness data for Marion Drain are presented in Table 16. Concentrations of dissolved copper ranged from 0.69 to 2.04 ug/L. Hardness data ranged from 76.2 to 143 mg/L. The highest concentrations of dissolved copper were in early April, July, and early August (Table 16). Hardness values were variable over the sampling period.

Table 16. Dissolved copper (ug/L) and hardness (mg/L) concentrations for Marion Drain.

Date	Dissolved Copper (ug/L)	Hardness (mg/L)
3/8/2012	0.69	143 J
3/20/2012	0.72	141
4/2/2012	0.97	94.6
4/18/2012	0.69	80.5
5/2/2012	0.80	82.0
5/16/2012	0.74	88.6
5/29/2012	0.71	76.2
6/12/2012	0.71	78.4
6/25/2012	0.73	74.1
7/9/2012	0.95	102
7/24/2012	2.04	94.3
8/8/2012	1.00	108
8/22/2012	0.81	90.6
9/4/2012	0.90	113

J: The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

Conventionals

Table 17 presents all of the data for the parameters used in the BLM that were collected from Marion Drain. All of the parameters, except pH and temperature, showed a decreasing pattern that ended in May and was followed by an increasing pattern. Temperature data show a seasonal pattern with cooler temperatures starting in the spring and maximum temperatures in August (Table 17).

Table 17. Conventional parameters for Marion Drain.

Date	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Alk (mg/L)	DOC (mg/L)	pH	Temp. (°C)
3/8/2012	34.7	13.6	24.3	4.22	15.7	16.3	144	2.2	8.7	9.5
4/2/2012	23.5	9.61	13.1	4.12	9.20	6.53	101	4.3	7.3	8.3
5/16/2012	21.3	8.50	10.6	2.53	8.23	5.01	94.8	2.0	8.0	15.0
5/29/2012	20.1	7.80	10.0	2.33	7.52	5.72	82.9	1.6	7.7	13.4
7/9/2012	23.5	8.89	11.8	2.88	10.5	6.90	102	2.1	7.5	19.6
8/8/2012	27.2	10.6	13.3	3.01	10.8	6.93	118	2.0	8.0	20.1
9/4/2012	28.2	11.2	13.7	3.35	11.9	6.46	123	1.8	8.2	18.2

Alk: Alkalinity
Ca: Calcium
DOC: Dissolved Organic Carbon
K: Potassium
Mg: Magnesium
Na: Sodium

Sulphur Creek Wasteway

Dissolved Copper and Hardness

Data for dissolved copper and hardness for Sulphur Creek Wasteway are presented in Table 18. Hardness data ranged from 84.0 to 296 mg/L. Dissolved copper concentrations ranged from 0.77 to 1.11 ug/L. Over the sampling period, dissolved copper concentrations were similar. The first and last sampling event had the highest concentrations (Table 18). Hardness data were variable over the sampling period.

Table 18. Dissolved copper (ug/L) and hardness (mg/L) concentrations for Sulphur Creek Wasteway.

Date	Dissolved Copper (ug/L)	Hardness (mg/L)
3/6/2012	1.11	296
3/20/2012	0.78	95.9
4/2/2012	0.86	93.5
4/18/2012	0.79	106
5/2/2012	0.86	109
5/16/2012	0.96	113
5/29/2012	0.80	84.0
6/12/2012	0.86	103
6/25/2012	0.77	73.7
7/9/2012	0.99	101
7/24/2012	0.99	99.0
8/8/2012	0.96	103
8/22/2012	0.90	110
9/4/2012	1.09	128

Spring Creek

Dissolved Copper and Hardness

Table 19 presents dissolved copper and hardness data for Spring Creek. Dissolved copper concentrations ranged from 0.74 to 1.4 ug/L. Hardness data ranged from 60.9 to 283 mg/L. Both dissolved copper and hardness varied over the sampling period. The highest concentration of dissolved copper was during the last sampling event (Table 19).

Table 19. Dissolved copper (ug/L) and hardness (mg/L) concentrations for Spring Creek.

Date	Dissolved Copper (ug/L)	Hardness (mg/L)
3/6/2012	0.79	283
3/20/2012	0.86	265
4/2/2012	0.93	99.1
4/18/2012	1.09	182
5/2/2012	0.91	74.3
5/16/2012	1.16	205
5/29/2012	0.80	60.9
6/12/2012	1.08	125
6/25/2012	0.74	54.8
7/9/2012	0.85	71.1
7/24/2012	1.03	135
8/8/2012	1.27	129
8/22/2012	1.12	103
9/4/2012	1.40	150

Discussion

Spatial Relationships

In general, the sites sampled in eastern Washington had lower dissolved copper concentrations than the sites sampled in western Washington. This difference can likely be attributed to climate. In eastern Washington agricultural areas, the climate is very dry and copper will not be used in the same way as western Washington where the weather is wet with mild temperatures (OWSC, 2013).

Copper, in terms of its use as a pesticide, is mainly used as a fungicide and an aquatic herbicide. One large use of copper in eastern Washington is in water conveyance systems to control aquatic algae and plants (Anderson, 2009). Use of copper in agricultural areas of western Washington is likely based on cropping patterns and weather (Kelly McLain, personal communication). Copper would likely be used to control fungus on fields before and after planting during wet spring weather and possibly before harvest, depending on weather.

The use of copper is dissimilar on the east and west sides of the state but also dissimilar within the western part of Washington. This variation can be attributed to the vastly different land-use patterns of central and southern Puget Sound and the Skagit-Samish basin in northern Puget Sound. Central and southern Puget Sound is dominated by dense urban land-use patterns while the Skagit-Samish basin in northern Puget Sound has mostly agricultural land use. With this dissimilarity in land use, a difference would be expected in the detection patterns between these areas.

Statistical Comparisons

To determine if there was a difference between the sites, data were tested for statistical differences in dissolved copper concentrations between the four sampled areas (Skagit, Urban, Yakima, and Wenatchee). Tested copper concentrations are shown in Figure 2, along with the associated Kaplan-Meier cumulative distribution functions (cdfs).

A non-parametric generalized Wilcoxon score test (also called the Peto-Prentice test) was used. This test determines whether distributions of two or more groups are the same, or if at least one is different (Helsel, 2005). It does not require the data to follow a specified distribution (such as log-normal). Distributions for the test are estimated using the Kaplan-Meier cdfs, which take into account non-detects at multiple detection limits. Tests were performed using the "cendiff" function in the Non-Detects and Data Analysis (NADA) package version 1.5-4 for R (R Core Team, 2013).

Wilcoxon score test results indicate at the 99% level that at least one of the areas had significantly different concentrations from the others. The p-value is approximately 1e-24, indicating that the null hypothesis of "no difference between areas" is very unlikely.

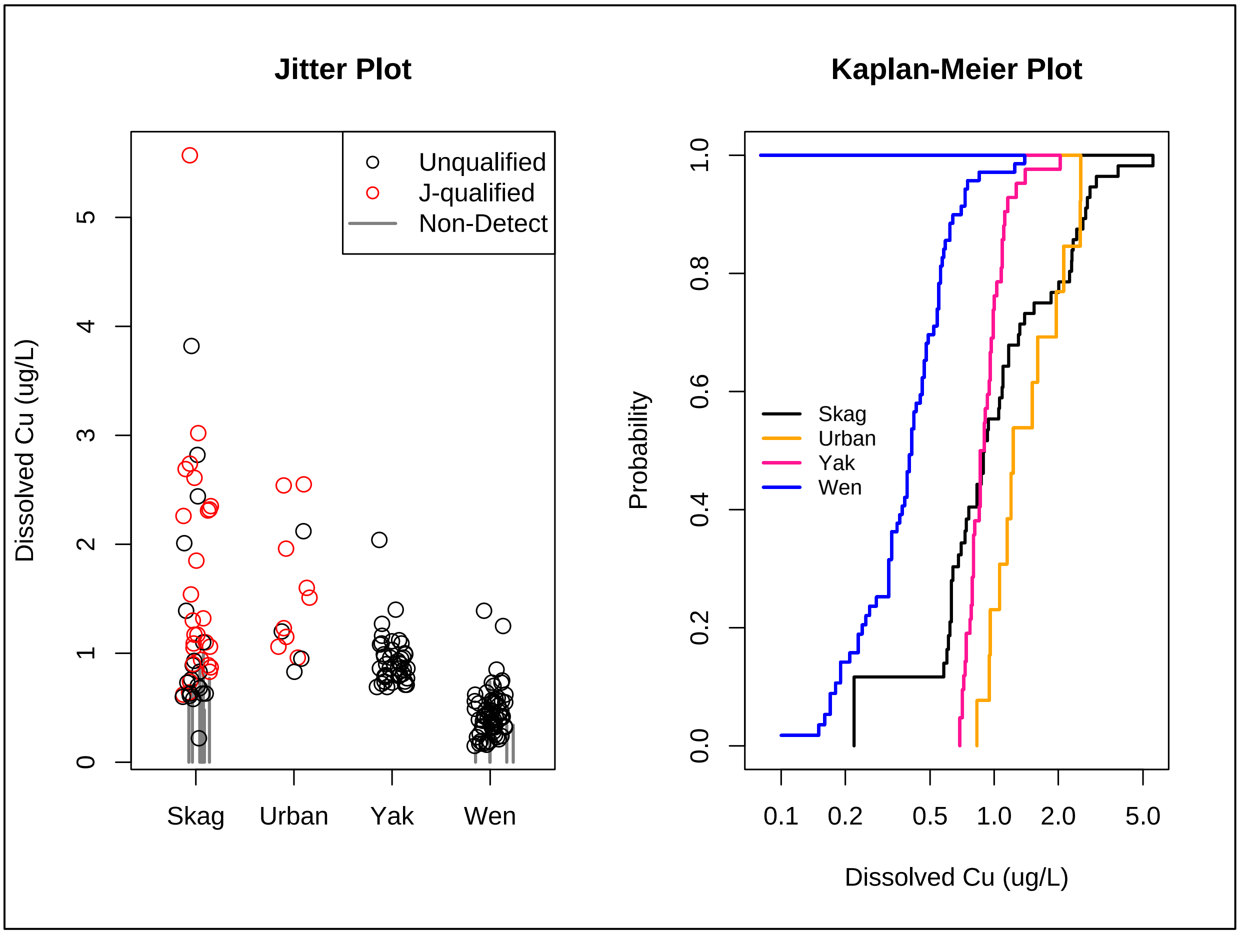

Figure 2. Tested copper concentrations shown in a jitter plot and the associated Kaplan-Meier cumulative distribution functions.

To determine which areas differ from the others the same test was run on all possible pairs of areas. Because multiple comparisons are being made, the error rate must be adjusted so that the overall error rate among all the comparisons remains correct. In this case, there are six comparisons possible between the four areas. A common formula for determining the individual error rate was used: Bonferroni’s formula which divides the overall error rate by the number of comparisons.

Test results among all possible pairs of areas found that the Wenatchee area was significantly lower than the other three areas, at the 99% level (p-value < 1e-16). The Yakima area was also found significantly lower than the Urban area at the 99% level (p-value < 1e-6). No significant difference was found between the Skagit-Yakima and Skagit-Urban area pairs. These results agree with the casual observation that none of the Kaplan-Meier curves cross each other, except for the Skagit.

It is noted that the urban area consists of a single site (Longfellow Creek) and therefore includes less data than the other three areas. The test results are valid for this site, but it is acknowledged the Kaplan-Meier cdf is less certain for this area than for the other three areas.

Detection Patterns

Longfellow Creek in Seattle and the Skagit-Samish basin sites had similar dissolved and total recoverable copper detection patterns. Starting in the spring most of the sampling sites had increasing copper concentrations that peaked in May and then again in late June. The amount was variable between sites with Longfellow Creek having the lowest concentrations. Brown Slough was the exception to the detection pattern seen at most sites. It had somewhat consistent concentrations of copper over the sampling period with a peak for the last sampling event in September. It also had the lowest concentrations out of the five western Washington sites.

The similarities in detection patterns between Longfellow Creek and most Skagit-Samish sites cannot be explained by land-use patterns. Sources of copper in urban environments are expected to be different from those in agricultural environments. The contribution of copper from brake dust washed off roadways is expected to be higher in Longfellow Creek than at the Skagit-Samish sites (Whiley, 2011). The contribution of other sources, such as homeowner use of products purchased at lawn and garden stores, are less clear. WSDA is currently conducting a copper use survey in the Puget Sound region and the results of the study should be helpful in evaluating the use of copper in urban and residential areas of Washington. In an agricultural environment, copper is used as a fungicide during wet weather to prevent damage to planted and growing crops.

Even though the uses and sources of copper are different in western Washington because of the differences in land use, the one thing that ties them together is weather. This is one factor that could possibly explain the similarity in detection patterns for the western Washington sampling locations.

Comparison to Other Data

Dissolved copper results are compared to historical data from Ecology's EIM system in Figure 3. Historical data from EIM were filtered to eliminate bias from results directly related to studies conducted in areas known to have metals contamination. The data collected for this study was compared to data collected in rivers and streams around the state. Data for this study were separated into two groups one for the western Washington sites and one for the eastern Washington sites. This was done because of the geographic and climatic differences between the two parts of Washington. Concentrations of dissolved copper from both areas fell within the range of the statewide data from EIM (Figure 3). Non-detect data were not used for these comparisons. The western Washington data fell on the higher side of the range with most of the data above the 50th percentile. Data from eastern Washington were on the lower side of the range with most of the data falling below the 50th percentile. Maximum dissolved copper concentrations for both sides of the state fell well below the maximum values seen in the historical statewide data (Figure 3).

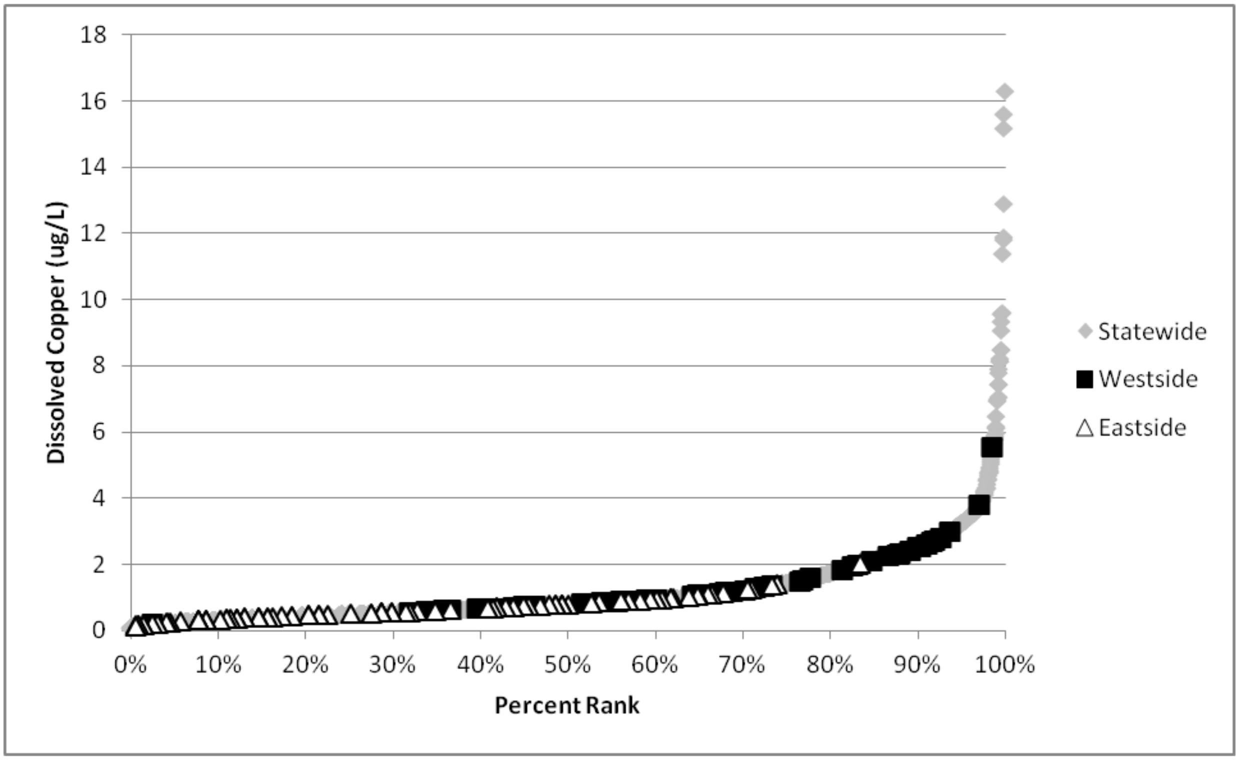

Figure 3. Percent rank of dissolved copper concentrations for project data (separated by geographic area) and data for the entire state from Ecology's Environmental Information Management (EIM) system.

Statewide n = 2364.

Total recoverable copper results from the five western Washington sites are compared to historical data from Ecology's EIM system in Figure 4. Historical data from EIM were filtered to remove non-detect data and to eliminate bias from results directly related to studies conducted in areas known to have metals contamination. The data collected for this study was compared to data collected in rivers and streams around the state. Concentrations of total recoverable copper fell within the range of the statewide data from EIM (Figure 4). A majority of the total recoverable copper for this 2012 study fell below the 80th percentile. Maximum total recoverable copper concentrations for this study are far below the maximum values seen in the historical statewide data (Figure 4).

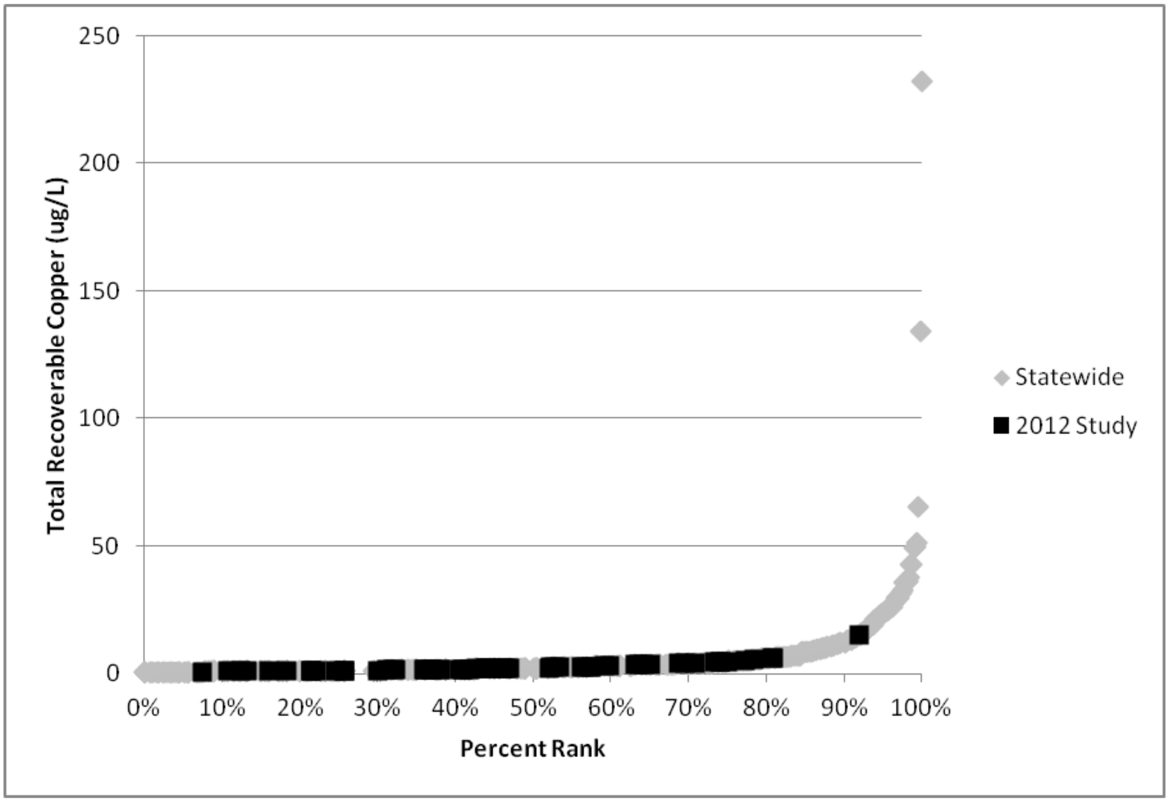

Figure 4. Percent rank of total recoverable copper concentrations for project data and data for the entire state from Ecology's Environmental Information Management (EIM) system.
Statewide n = 444.

Loading

Loads of copper were calculated for the five western Washington drainages using this formula: discharge (Q) in cubic feet per second (cfs) x total recoverable copper concentration in parts per million (ppm) x 5.4 = pounds/day (Kittrell, 1969). All copper data were reported by the MEL in parts per billion (ug/L). The copper data used in the above equation were converted to ppm (mg/L) for use in the equation. Any estimated loads are discussed in the associated section and are marked in the appropriate figures.

Urban Drainage

Longfellow Creek

Longfellow Creek is the lone sampling location in central Puget Sound. It is located in West Seattle and represents an urban drainage basin. Most of the land use in the area is residential and commercial development (Sargeant et al., 2013). However, the creek flows through West Seattle Golf Course and near its confluence with the West Duwamish Waterway flows through an industrial area.

All total recoverable copper concentrations from Longfellow Creek were low (Table 3). Small amounts of copper coupled with low discharge volumes resulted in small amounts of copper entering the West Duwamish Waterway (Figure 5). A spike in copper loading can be seen in May. This spike was associated with an increase in discharge from a storm event that occurred on the day of sampling. The copper detection from this day was also the highest for Longfellow Creek during the study period (Table 3). A spike in loading from a storm event likely indicates storage and washoff of copper, which may be related to usage in the watershed. Spikes in loading during storm events also show that rainfall is an important factor driving loading.

Two dates at the end of the sampling period are missing load calculations because of censored total recoverable copper data discussed earlier.

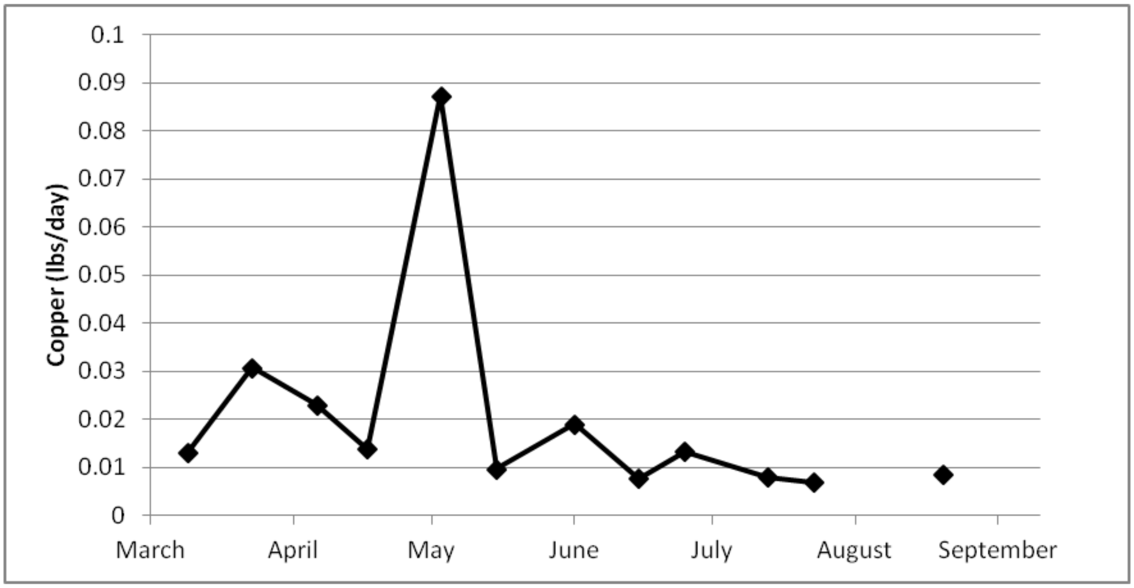

Figure 5. Calculated copper loads for Longfellow Creek, March through September, 2012 (lbs/day).

Western Washington Agricultural Drainages

In western Washington agricultural areas, copper is used as a fungicide during wet weather. Of most importance to agriculture is the wet weather in the spring when crops are being planted and are beginning to grow. Use of copper will depend on the types of crops being grown in a particular watershed. Crops grown in a particular watershed often vary from year to year, so copper use may vary from year to year as well. How much copper reaches a creek, river, or slough will depend on weather, cropping patterns, and the amount of cultivated land that drains to a particular waterway.

In 2012, the weather was an important factor in copper use and loading in the Skagit-Samish basin. Higher than average rainfall in the spring and early summer (AWN, 2013) most likely led to the use of copper to control fungus on certain crops. Data from an AgWeatherNet (AWN) weather station near Mount Vernon shows that average precipitation (1994-2011) in the area during the spring was 7.87 inches and the month of June average precipitation for the same time period was 1.76 inches (AWN, 2013). During 2012, precipitation during the spring was 10.47 inches and in the month of June was 3.15 inches (AWN, 2013).

Samish River

The Samish River is the largest water course that was studied for copper loading to Puget Sound. Like the water in all of the other agricultural sampling locations, the Samish River discharges to Northern Puget Sound, specifically Samish Bay. Most of the lower portion of the Samish River runs through agricultural land. There are a number of crops that are grown in the basin as well as other types of agriculture including dairy farming (Sargeant et al., 2013).

All of the total recoverable copper concentrations from the Samish River were low (Table 5). Water volumes, especially early in the year, were many times larger than the rest of the Skagit-Samish sampling sites combined. Even though only small amounts of copper were seen in the Samish River (Table 5), the volume of discharge made the loads higher than other sites. As would be expected, the highest loads were seen in April and May when the largest discharge was measured at the Samish River. These higher discharge volumes were associated with rain events that occurred prior to and on the day of sampling. Outside of the peak in April and May, there are two smaller peaks in March and late June. Both of these have storm events that occurred in a similar timeframe as the other peak loads.

In the spring (March – May) most copper use is on berries and some vegetables (Kelly McLain, personal communication). There are many kinds of berries and vegetables that are grown in the Samish River watershed (Sargeant et al., 2013). The spike seen in late June is potentially due to copper use from above-average rainfall in June (AWN, 2013). During this time, copper could have been used as a fungicide on a number of vegetable and some seed crops.

For the time period of this study, slightly more than half of the discharge volumes used in the loading calculations are based on a rating curve. Those loads that are based on estimated volumes of water are themselves considered to be estimates. Loads based on estimated discharge volumes are indicated in Figure 6.

The last load calculation is missing due to data censoring of total recoverable copper discussed earlier.

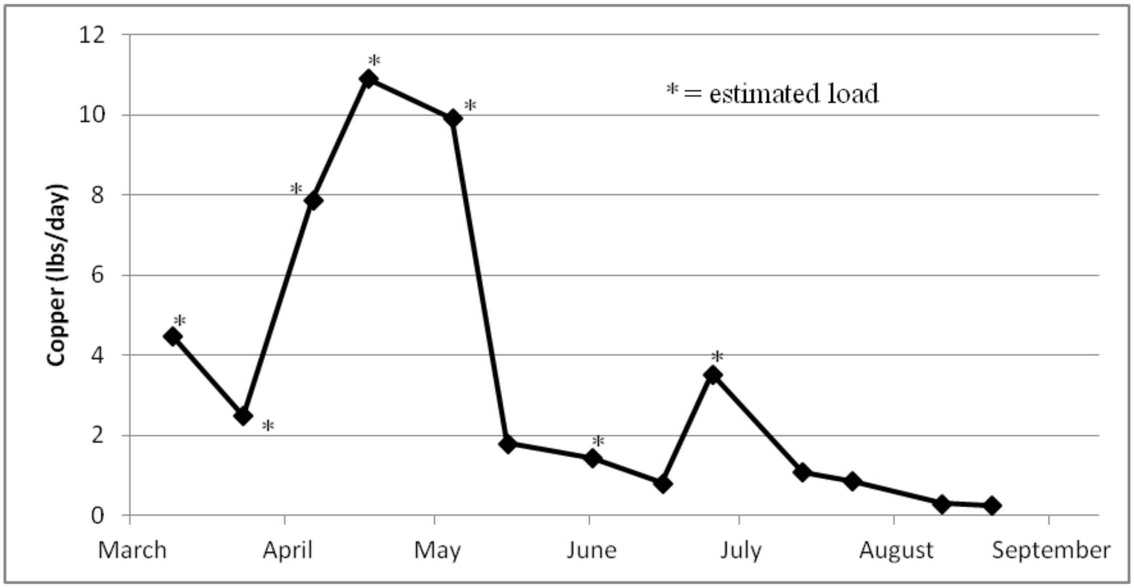

Figure 6. Calculated copper loads for the Samish River, March through September, 2012 (lbs/day).

Brown Slough

Brown Slough drains agricultural land on Fir Island and discharges into Skagit Bay in Northern Puget Sound. A wide variety of crops are grown in the Brown Slough basin (Sargeant et al., 2013).

Like the Samish River, total recoverable copper concentrations for Brown Slough were low (Table 7). Water volumes at Brown Slough generally decreased over the sampling period. There was one discharge measurement that was higher than most that occurred in mid-May. This discharge event may have been tied to a previous storm event that increased runoff in the drainage basin. Small discharge volumes and concentrations of total recoverable copper resulted in small copper loads to Skagit Bay from Brown Slough (Figure 7). The peak discharge measurement seen in mid-May is reflected by the spike in copper loading (Figure 7).

As was discussed in the Samish River section, copper is used primarily on berries in the spring and also some on vegetables. In the Brown Slough watershed, a small amount of berries are grown along with a wide variety of vegetables. Copper use on berries and vegetables could possibly explain spikes in loading seen in the spring. The limited amount of berries is one potential reason for the small amounts of copper and low copper loads seen in Brown Slough.

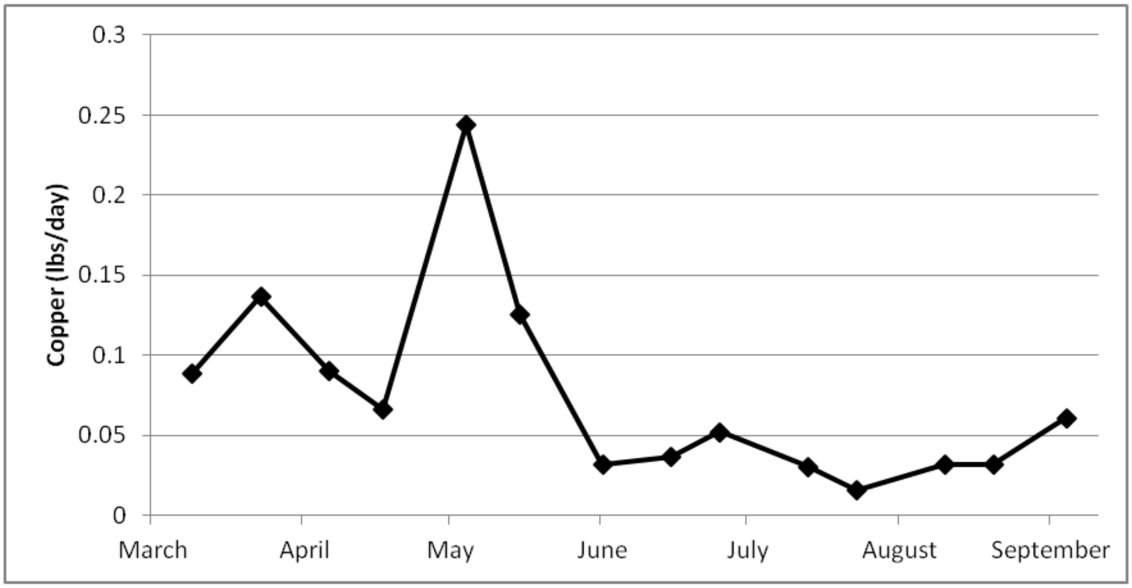

Figure 7. Calculated copper loads for Brown Slough, March through September, 2012 (lbs/day).

Indian Slough

Indian Slough drains a portion of the Northern Skagit River delta and discharges into Padilla Bay in Northern Puget Sound. Much of the drainage area of Indian Slough is dominated by agriculture and supports a number of different crops (Sargeant et al., 2013).

Some total recoverable copper concentrations for Indian Slough were higher than those from the other Skagit-Samish basin sampling sites. After the beginning of May, most detections were several times lower than earlier in the season (Table 8). Discharge measurements were fairly stable over the sampling period with some fluctuation in the first few months. Highest discharge volumes were seen in the beginning of the sampling period. The total recoverable copper concentrations and the discharge volumes in the early part of the sampling period resulted in higher loads of copper from March through early May than were seen from mid-May through September (Figure 8). There was one exception to this in late June. This increase in copper loading in late June coincides with the spike in total recoverable copper (Table 8).

A large part of the cropped area of Indian Slough is in berry and potato production as well as other vegetables and seeds (Sargeant et al., 2013). In the spring, copper is used mainly on berries, with some additional use on vegetables (Kelly McLain, personal communication). The wetter than average spring and early summer (AWN, 2013) could explain the copper loading especially in late July when copper is not normally used.

The last load calculation for September is missing because of data censoring that was discussed earlier.

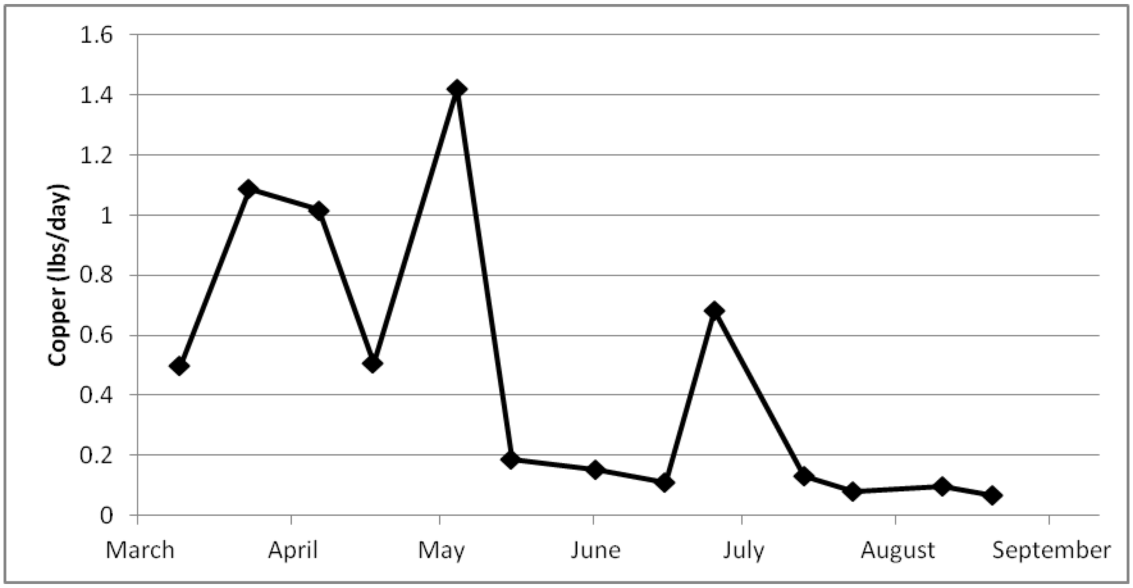

Figure 8. Calculated copper loads for Indian Slough, March through September, 2012 (lbs/day).

Downstream Big Ditch

Downstream Big Ditch drains a large area in the southern part of the Skagit River delta and discharges into Skagit Bay. The upper watershed is made up primarily of forested lands. The middle of the watershed flows through the city of Mount Vernon. The land use in this area is residential, commercial, and light industrial (Sargeant et al., 2013). The lower part of the watershed, where sampling occurred, is made up solely of agriculture. A large number of crops are grown in the lower watershed (Sargeant et al., 2013).

Over the sampling period, downstream Big Ditch had the highest total recoverable copper concentrations out of all of the sampling locations (Table 9). Concentrations of total recoverable copper peaked in early May and then decreased over the rest of the sampling period. Discharge volumes at downstream Big Ditch were similar to those from Indian Slough.

Loads of copper over the sampling period are shown in Figure 9. There appears to be a decreasing pattern of copper loading from March to September with a spike in loading in early May. This spike can be attributed to the highest detection of total recoverable copper as well as a large volume of water. A streamflow measurement was not able to be obtained on that day due to high water volume. Instead the highest flow that was obtained for the sampling period was used (previous week flow measurement). Since the actual discharge volume was not used in the loading calculation the load for the 5/4/2012 sample event is considered an estimate. The actual load of copper is likely higher because the discharge volume would have been higher if a measurement could have been obtained. The final load calculation for September is missing because of data censoring, as discussed in the Quality Assurance section.

As has been discussed in previous sections, copper is used primarily on berries in the spring, along with use on some vegetables. The Big Ditch watershed has very little berry production but has a large number of vegetables that are produced. Since copper is more often used on berries than on vegetables, detections of copper and subsequent loads do not completely match up. Big Ditch is unique among the agricultural ditches that were sampled for this study. It is the only waterway that is influenced by residential and light industrial land use and flows adjacent to Interstate 5 for several miles.

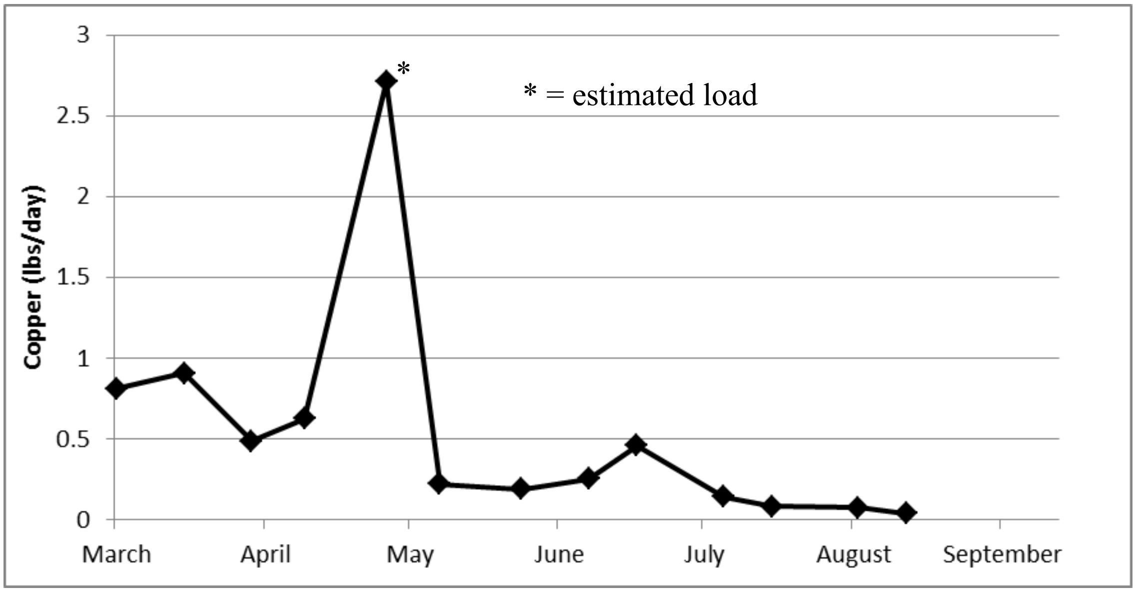

Figure 9. Calculated copper loads for downstream Big Ditch, March through September, 2012 (lbs/day).

Comparison of the Washington State Water Quality Criteria to the Biotic Ligand Model

Washington State Criteria

Washington State's current approach for calculating water quality criteria is promulgated in the Washington Administrative Code (WAC) Chapter 173-201A Section 240 (WAC, 2006). This approach, based on hardness, was recommended for use by the EPA in 1985. The Washington State approach uses regressions of toxic concentrations of copper against hardness (over a large range) to set criteria for the protection of aquatic organisms (EPA, 2007). It is important to note that these regressions were not limited to hardness. Also included were pH and alkalinity.

Limitations of the Washington State Approach

Even though the regressions include water quality factors that influence bioavailability and toxicity beyond hardness, the regressions are most useful when applied to waters with similar conditions (EPA, 2007). In addition, the regressions do not take into account other factors that affect toxicity of metals. These factors include dissolved organic carbon (DOC), metal speciation, and overall ionic strength.

Comparison to Measured Concentrations

Freshwater quality criteria for copper are calculated based on the hardness at each sampled location. The acute criteria are calculated using the formula $(0.960)(e^{(0.9422[\ln(\text{hardness})]-1.464)})$ and chronic criteria are calculated using the formula $(0.960)(e^{(0.8545[\ln(\text{hardness})]-1.465)})$. Marine water quality criteria are not based on the hardness of the sampled water. Instead there are static values for acute and chronic water quality criteria in marine water.

All of the sites sampled for this study, except one, are considered freshwater and were compared to the Washington State acute and chronic water quality criteria for copper. Brown Slough is considered to be a marine water site (Sargeant et al., 2010) and was compared to the acute and chronic marine water quality criteria of 4.80 and 3.10 ug/L, respectively.

All of the results for the dissolved copper samples, except for one, were below any Washington State water quality criteria (Appendix C, Table C1, 3, 5-7, 9, 10-13, 14, 16 and 17). One sample from Brown Slough was above the marine chronic water quality criteria of 3.10 ug/L. The sample was collected on 9/4/2012 and the dissolved copper concentration was 3.82 ug/L (Appendix C, Table C-5).

Biotic Ligand Model (BLM) Criteria

In 2007, EPA issued an updated recommendation for calculating copper water quality criteria. This new recommendation calls for the use of the BLM to calculate site specific acute and chronic water quality criteria for copper in freshwater environments. This most recent update in recommended water quality criteria for copper takes into account new toxicity data and addresses the limitations of the Washington State hardness-based approach (EPA, 2007).

Advantages of the BLM

The BLM predicts copper toxicity after taking into account complexation with DOC and inorganic ligands (carbonate, bicarbonate, and hydroxides), competition with other earth metals, and speciation of copper (HydroQual, 2007). The BLM uses ten parameters to account for complexation, competition, and speciation. These ten parameters are water temperature, pH, DOC, alkalinity, sulfate, chloride, calcium, magnesium, sodium, and potassium.

Temperature is not directly related to the toxicity of copper but it does impact the rates of reactions. Reactions can speed up or slow down based on temperature. For example, warmer temperatures could increase the toxicity of copper because absorption by organisms is accelerated (Lemus and Chung, 1999).

pH has a large impact on the interaction of metals with the environment. Chemical speciation of copper, and other metals, is directly related to pH (HydroQual, 2007). With increases in pH, the amount of copper that complexes with carbonate increases, which, in turn, decreases toxicity (Di Toro et al., 2001). pH is also important in determining how much DOC can complex with copper (HydroQual, 2007). DOC can be a critical factor in the bioavailability of copper (HydroQual, 2007). This is because DOC complexes with copper which makes it unavailable to organisms. As the amount of DOC increases, more copper is needed to cause the same level of toxicity (Di Toro et al., 2001).

In addition to forming complexes with DOC, copper also complexes with inorganic carbon. Some forms of inorganic carbon include carbonate and bicarbonate. Analysis for dissolved inorganic carbon is not often included in sampling programs but can be estimated using alkalinity and pH (HydroQual, 2007).

Sulfate and chloride are not as critical as some of the other components of the BLM input but they do play an important role in the forming of complexes through charge balance and ionic strength (HydroQual, 2007).

Several earth metals that are naturally occurring in most waterways compete with copper at binding sites. Increases in concentrations (i.e., ionic strength) of the metals calcium, magnesium, sodium, and potassium correspond with a decrease in toxicity of copper (HydroQual, 2007). Calcium and sodium are the most important earth metals that compete with copper. Magnesium plays a lesser role, but for some organisms it may be a critical component of competition (HydroQual, 2007). Potassium does not have a direct affect on copper toxicity but could have a future application in the BLM.

Limitations of the BLM

Currently, the BLM does not require the input of sulfide concentrations based on the assumption that sulfide in natural waters is negligible. Recent research has shown that this assumption may not be true (HydroQual, 2007). Sulfide has a strong attraction to copper and other metals, and it could play an important part in speciation and complexation.

Aquatic toxicity from metals like copper can be significantly reduced by complexation with DOC. DOC is made up of terrestrial (humic) and aquatic (fulvic) based acids (HydroQual, 2007). The BLM takes into account the entire makeup of DOC. Unfortunately, most laboratories do not quantify the composition of DOC. It is assumed that the majority of DOC in aquatic environments is fulvic acid, so a default of 10% humic acid is entered into the BLM (HydroQual, 2007). It has been shown that the differences in forms of DOC have a large effect on the amount of protection to aquatic organisms (Wood et al., 2011). The true degree of protection that DOC provides will not be fully characterized in the BLM unless accurate measurements of the composition of DOC are input into the BLM.

It is also important to note that the BLM is a complex mathematical model that uses thermodynamics and water quality parameters to predict toxicity. Results from the BLM cannot be applied without an understanding of how the model works and its limitations.

Comparison to Measured Concentrations

Data for dissolved copper from the four selected sampling sites were compared to BLM water quality criteria. Version 2.2.3 of HydroQual's BLM was used to calculate the water quality criteria. None of the dissolved copper concentrations from the samples collected at Longfellow

Creek, Samish River, Wenatchee River, and Marion Drain were above the BLM water quality criteria (Appendix C, Table C-2, 4, 9, and 15).

Comparison of Washington State and BLM Criteria

As would be expected, there were similarities between the Washington State water quality criteria and the BLM results in areas with similar ionic strengths. Longfellow Creek and Marion Drain had similar data for the BLM water quality parameters as well as hardness (Tables 3, 4, 16, and 17). Data from the Samish and Wenatchee Rivers were similar for the BLM water quality parameters and hardness (Tables 5, 6, 10, and 11), but were much lower than those from Longfellow Creek and Marion Drain.

While overall the water quality parameters for Longfellow Creek and Marion Drain as well as the Samish and Wenatchee Rivers were similar, the calculated water quality criteria varied from site to site (Appendix C, Table C-1 through C-4, C-8, C-9, C-14 and C-15). The Washington State criteria were directly related to hardness. Increases in hardness showed corresponding increases in acute and chronic water quality criteria. This occurrence was expected because of how the Washington State criteria are derived. Lack of similarity in the BLM results can likely be attributed to the complex interactions between the different water quality parameters that affect the bioavailability and toxicity of copper in the aquatic environment.

Results show no discernible difference geographically between sites from the eastern and western parts of the state. Instead, differences were attributed to the specific water quality parameters that control the bioavailability and toxicity of copper, most notably the ionic strength and amount of DOC in the water. These conditions were variable at all of the sites no matter where the sampling locations were in the state.

Longfellow Creek

From March to June, Washington State water quality criteria and the BLM-recommended acute and chronic water quality criteria were similar (Figures 10 and 11). In July and September, Washington State acute and chronic water quality criteria were much higher than those for the BLM. This change is likely attributed to a drop in DOC (Table 4). As was described in earlier sections, DOC plays an integral role in the bioavailability of copper. Copper forms complexes with DOC which makes it unavailable biologically (Di Toro et al., 2001). Since there is less DOC present in July and September, the BLM would predict lower (more protective) water quality criteria.

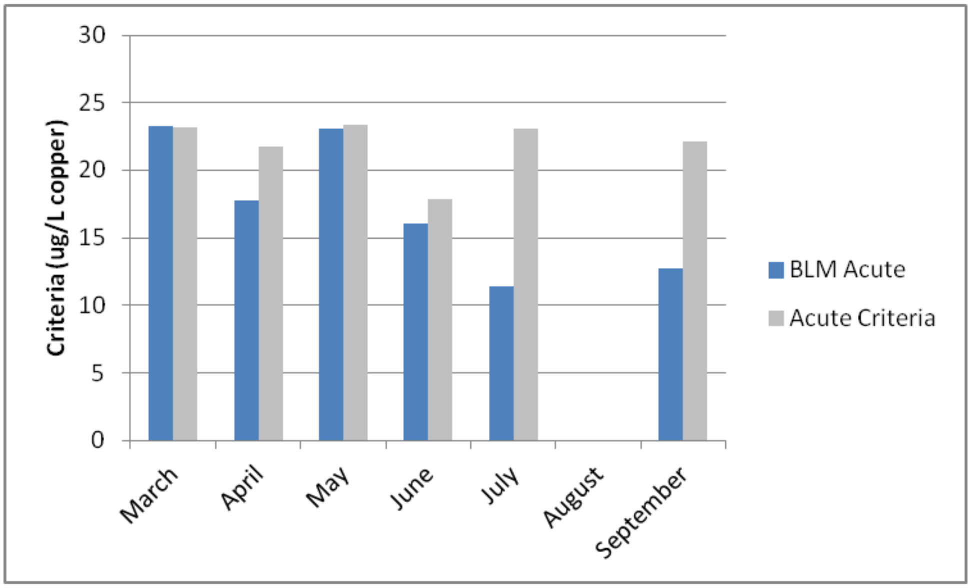

Figure 10. Washington State and BLM-recommended acute water quality criteria (ug/L) for Longfellow Creek.

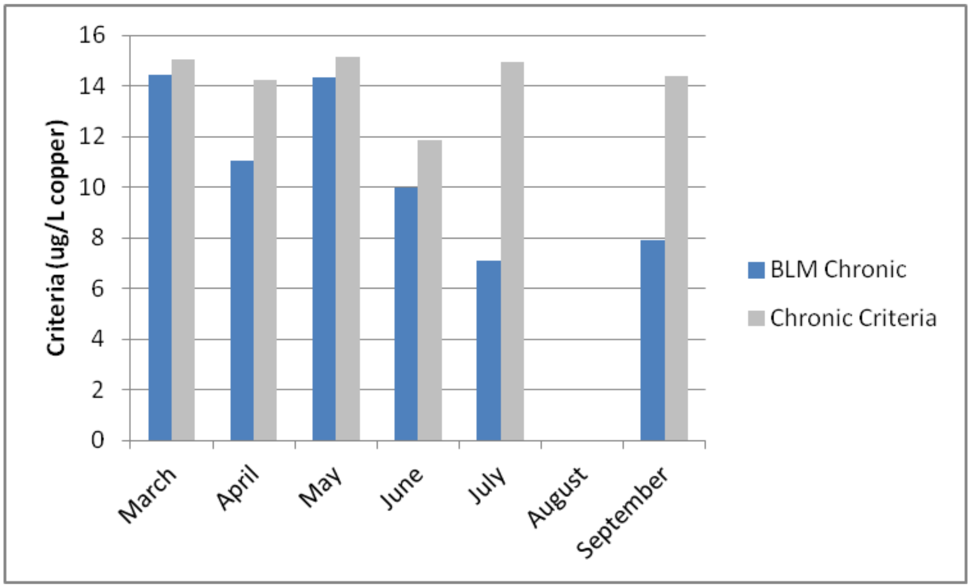

Figure 11. Washington State and BLM-recommended chronic water quality criteria (ug/L) for Longfellow Creek.

Marion Drain

All of the months, except June and July, had similar Washington State and BLM-recommended acute and chronic criteria (Figures 12 and 13). The BLM chronic water quality values for June and July were quite a bit lower than the State criteria. Differences seen in these two months cannot be attributed to a single reason.

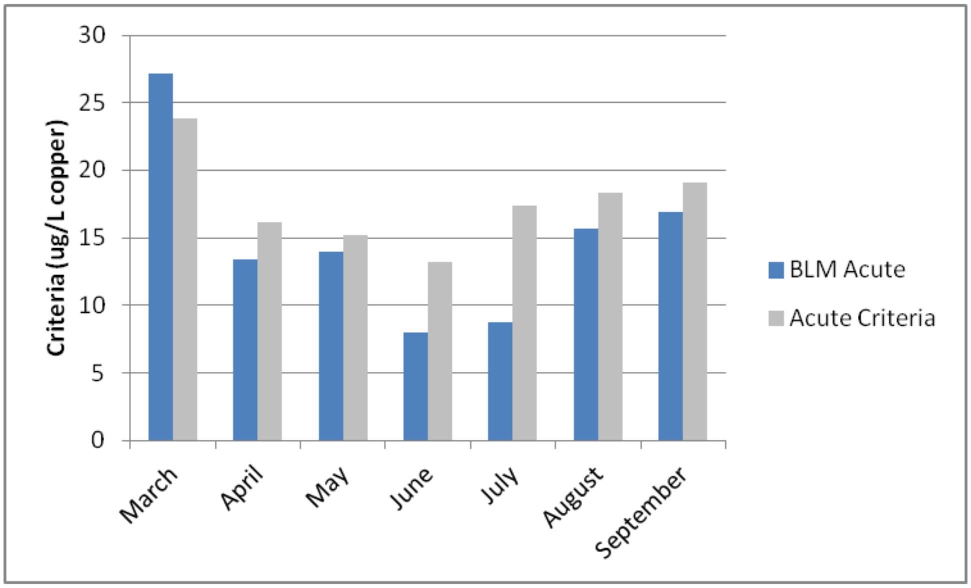

Figure 12. Washington State and BLM-recommended acute water quality criteria (ug/L) for Marion Drain.

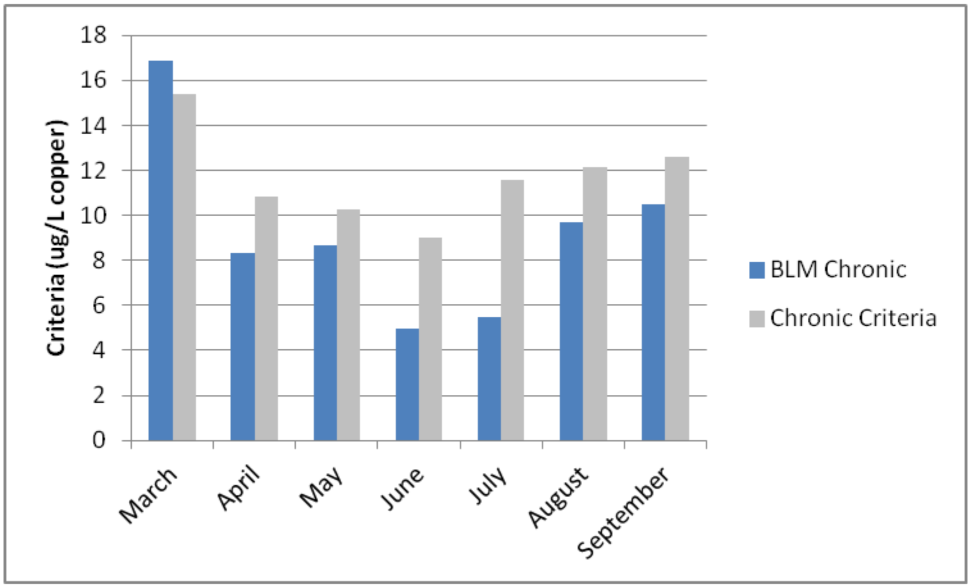

Figure 13. Washington State and BLM-recommended chronic water quality criteria (ug/L) for Marion Drain.

In June, the difference likely was caused by low DOC and an overall decrease in ionic strength from previous sampling events (Di Toro et al, 2001). These two factors taken together made copper more bioavailable, which would account for the BLM-recommended criteria being lower (more protective). For July, the difference between the two methods likely can be attributed to low pH and to a lesser extent low DOC. Low pH reduces the speciation of copper to non-biologically available forms and copper complexation with DOC (Di Toro et al., 2001). A low pH coupled with low DOC makes copper more biologically available. This would explain the higher degree of protection from the lower recommended acute and chronic criteria produced by the BLM.

Samish River

All of the months, except March, had similar Washington State acute and chronic water quality criteria and BLM-recommended acute and chronic water quality criteria (Figures 14 and 15). The State criteria for March were quite a bit lower than the BLM criteria. The reason for this difference is not readily apparent. It is most likely DOC that accounts for the difference. Hardness is low but the DOC appears to offset lower competition in the BLM, which allows for more copper to be present.

It is also important to note that the temperature for March and April are outside the calibration range of the model. Temperature is important because it controls reaction rates associated with the model (HydroQual, 2007). Since the temperatures are outside the calibration range of the model, the associated water quality criteria may not be reliable.

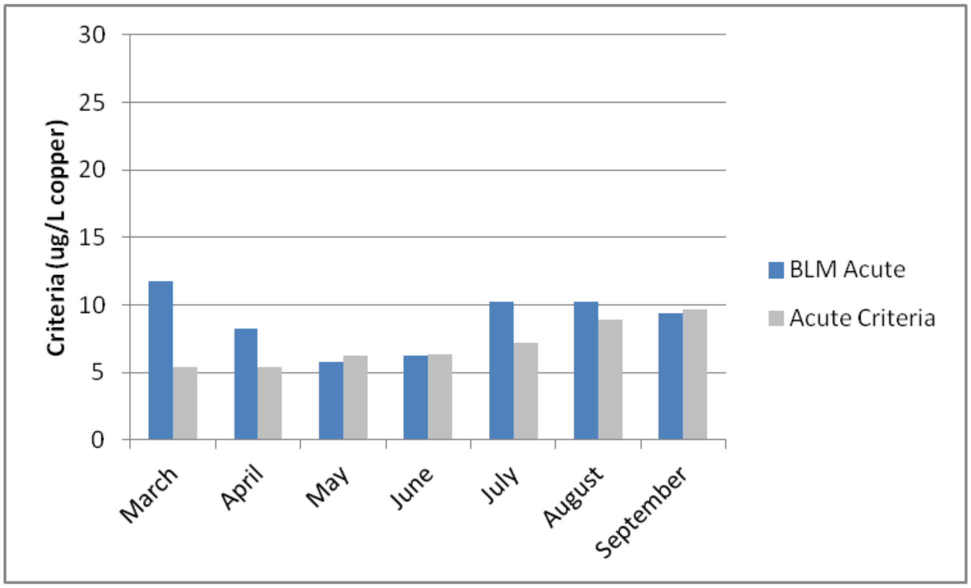

Figure 14. Washington State and BLM-recommended acute water quality criteria (ug/L) for the Samish River.

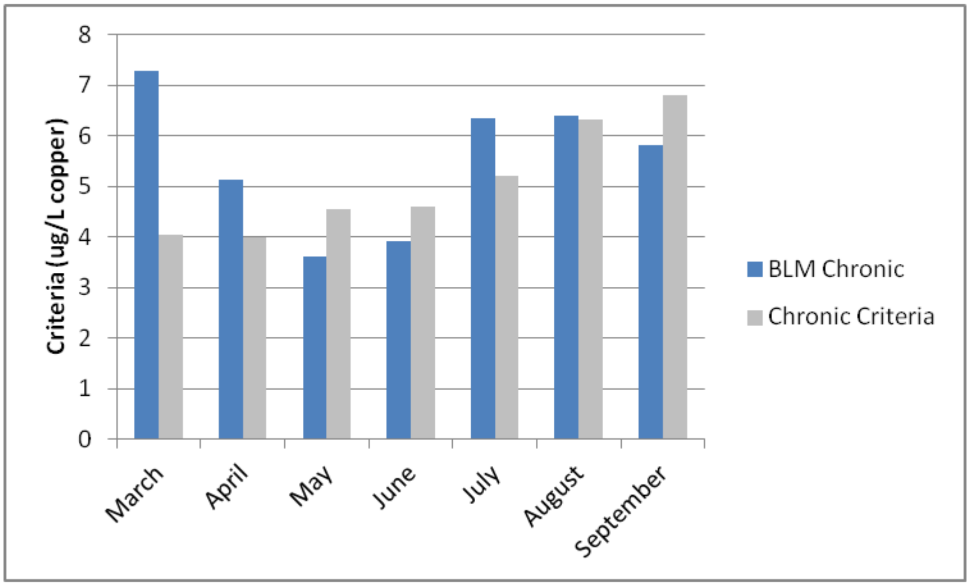

Figure 15. Washington State and BLM-recommended chronic water quality criteria (ug/L) for the Samish River.

Wenatchee River

Three of the sampling months (March, April, and September) have BLM-recommended acute and chronic water quality criteria that are quite a bit higher than the Washington State acute and chronic water quality criteria (Figures 16 and 17). Acute and chronic criteria for both the State and BLM are similar for May through June. The differences in March and April likely are related to pH and alkalinity as well as overall ionic strength. For April, DOC likely plays an additional role in reducing the bioavailability of copper.

Like with the Samish River, there are some temperatures for the Wenatchee River that are outside the calibration range of the BLM (Table 11). In this case, March through June temperatures were below the lower bound of the calibration range. It is unknown what effect the low temperatures have on the model. With temperatures outside the calibration range of the model, the associated water quality criteria may not be reliable. Therefore, it cannot be said with certainty that the BLM is being less protective than the Washington State hardness-based calculation.

Outside of the differences seen in March and April, there is a large difference between the BLM-recommended acute and chronic water quality criteria and the Washington State acute and chronic water quality criteria in September (Figures 16 and 17). The BLM criteria are much higher than the State criteria. Like in March and April, the overall ionic strength coupled with alkalinity and pH likely is the reason for the difference. The higher ionic strength with increased alkalinity and pH creates more competition at the biotic ligand as well as increased speciation and complexation of copper. All of this taken together allows the BLM to calculate less protective recommended water quality criteria.

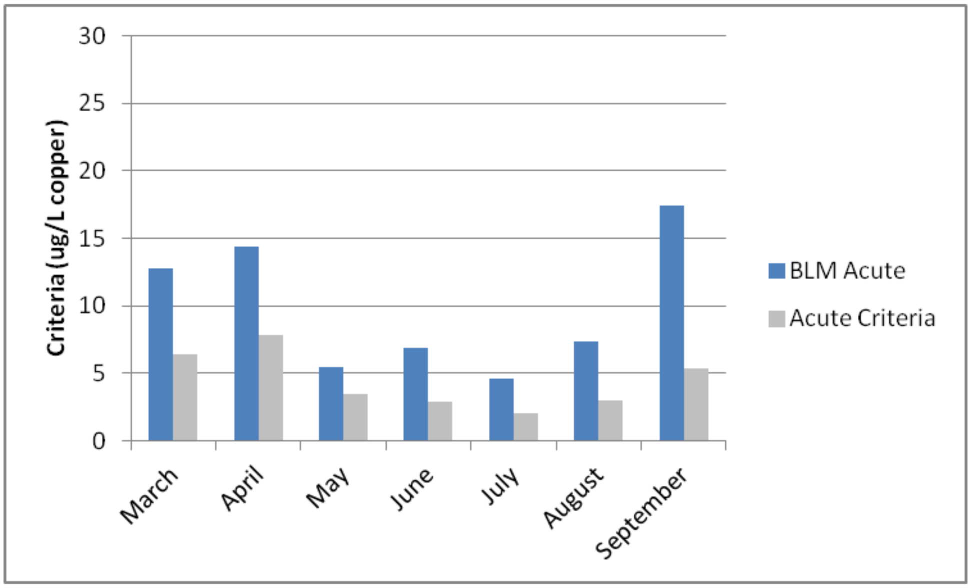

Figure 16. Washington State and BLM-recommended acute water quality criteria (ug/L) for the Wenatchee River.

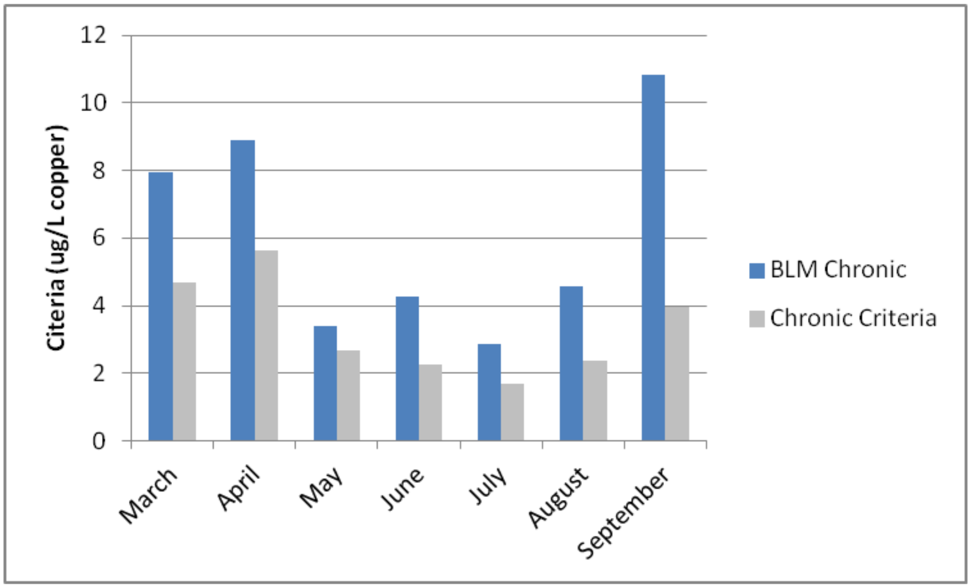

Figure 17. Washington State and BLM-recommended chronic water quality criteria (ug/L) for the Wenatchee River.

Statistical Comparison of Washington State and BLM Water Quality Criteria

The statically assess differences between the Washington State water quality criteria and the BLM-recommended water quality criteria a Wilcoxon Rank-Sum test was run on the data. This statistical test is a hypothesis test that compares two independent variables. The null hypothesis for this study is: the median of the difference between the BLM and State water quality value is zero. The null hypothesis is rejected when the p-value from the test is <0.05.

Data from the BLM and State water quality calculation were tested for a significant difference between the results from the two methods. The values were tested separately in order to avoid the assumption that both the acute and chronic water quality criteria would have the same outcome.

When all four sites were combined, the Wilcoxon Rank-Sum test found no difference between the BLM and the Washington State equation for either acute or chronic values. When acute water quality values for the entire sampling period from all four sites were combined (n = 28), the p-value was 0.99 at the 95% confidence level. Since the p-value is greater than 0.05, the null hypothesis was not rejected for the acute values. Chronic water quality values were analyzed the same way as the acute water quality values. The result was a p-value of 0.36 at the 95% confidence level; therefore the null hypothesis was not rejected for the chronic values.

To further test the data, the four sites were split into two groups based on similar water quality data. The Wilcoxon Rank-Sum test showed a significant difference between the Washington State and BLM-recommended water quality criteria for sites with similar water quality conditions. The tested groups had p-values less than 0.05 at the 95% confidence interval (Table 20). These p-values allow for the rejection of the null hypothesis. This shows that the median difference between the BLM and State acute and chronic water quality criteria is likely not zero.

Table 20. Wilcoxon Rank-Sum test results for sites with similar water quality data.

Locations	n	p-value	Sigificant at 95 percent confidence interval
Acute			
WE-1 and SR-1	14	0.007	yes
MA-2 and LC-1	14	0.001	yes
Chronic			
WE-1 and SR-1	14	0.002	yes
MA-2 and LC-1	14	0.004	yes

LC-1: Longfellow Creek
MA-2: Marion Drain
SR-1: Samish River
WE-1: Wenatchee River

Marion Drain and Longfellow Creek had similar water quality conditions and the statistical test showed that the BLM-recommended water quality criteria is significantly lower (1.3 to 6.4 ug/L)[2] than the Washington State water quality criteria. The Samish and Wenatchee Rivers also had similar water quality conditions. However, instead of being significantly lower than the State criteria, the BLM criteria was significantly higher (1.5 to 5.4 ug/L)[2].

---

[2] 95% confidence interval for median difference.

Conclusions

Results of this 2012 study support the following conclusions.

- Dissolved copper concentrations were generally higher in western Washington than in eastern Washington.
- Results from the eastern and western Washington sampling locations likely differed based on weather related to geographic location and differences in application of copper related to land use. In eastern Washington, copper is mainly used in agricultural water conveyance systems before and during the irrigation season to control algae and aquatic plants. In western Washington agricultural areas, copper is used during wet weather as a fungicide on several different crops.
- At the five western Washington drainages, loading of total recoverable copper was slightly lower in summer than when sampling began in the spring. This is likely due to decreasing precipitation and smaller water volumes from the spring to summer.
- One sample from Brown Slough was above (did not meet) the Washington State marine chronic water quality criteria. No other samples were above any Washington State water quality criteria or BLM-recommended water quality criteria.
- Differences between the State criteria and the BLM criteria were not related to geographical location (western vs. eastern Washington). Instead, differences were attributed to site-specific water quality conditions, namely the ionic strength (calcium, sodium, magnesium, sulfate, and chloride) of the water and amounts of DOC.
- Statistical tests showed significant differences between the BLM-recommended criteria and the Washington State criteria at various sites. At Marion Drain and Longfellow Creek, BLM acute and chronic criteria were significantly lower than the State criteria. At the Samish and Wenatchee Rivers, the BLM acute and chronic criteria were significantly higher than the State criteria.

Recommendations

Results of this 2012 study support the following recommendations.

- Sample copper during rain events or during the wet time of year in western Washington. Most of the sampling from this study occurred during the months when there is typically little precipitation. Sampling in the wet season could provide valuable data for assessing the true amount of copper entering Puget Sound.
- Sample copper for a year in both urban and agricultural areas to assess whether application of copper-containing pesticides is a factor in detection patterns.
- Evaluate the usage data from the Washington State Department of Agriculture survey in the context of water quality results from this study. This evaluation could provide valuable information about detection patterns and guide sample timing in future studies.
- Provide funding to Manchester Environmental Laboratory for method development to characterize the composition of dissolved organic carbon (i.e., the proportion of fulvic acid vs. humic acid). This would allow for increased accuracy in the Biotic Ligand Model.

References

AgWeatherNet. The Washington Agricultural Weather Network Version 2.0, Washington State University Prosser, Washington, Daily Precipitation (inches). http://weather.wsu.edu/awn.php. Viewed July 25, 2013.

Anderson, P. D., and D. Sargeant, 2009. Addendum 3 to Quality Assurance Project Plan: Washington State Surface Water Monitoring Program for Pesticides in Salmonid Habitat for Two Index Watersheds. Washington State Department of Ecology, Olympia, WA. Publication No. 03-03-104ADD3. https://fortress.wa.gov/ecy/publications/summarypages/0303104ADD3.html

Anderson, P. D., 2009. Irrigation Canal Effects on Copper Levels in Water and Sediment of the Mid-Columbia and Wenatchee Rivers. Washington State Department of Ecology, Olympia, WA. Publication No. 09-03-005. https://fortress.wa.gov/ecy/publications/summarypages/0903005.html

Anderson, P. D., 2011. Addendum 4 to Quality Assurance Project Plan: Washington State Surface Water Monitoring Program for Pesticides in Salmonid Habitat for Two Index Watersheds. Washington State Department of Ecology, Olympia, WA. Publication No. 03-03-104Add4. https://fortress.wa.gov/ecy/publications/summarypages/0303104ADD4.html

Anderson, P. D., 2012. Addendum 5 to Quality Assurance Project Plan: Washington State Surface Water Monitoring Program for Pesticides in Salmonid Habitat for Two Index Watersheds. Washington State Department of Ecology, Olympia, WA. Publication No. 03-03-104-Addendum 5. https://fortress.wa.gov/ecy/publications/summarypages/0303104Addendum5.html

Burke, C. and P. Anderson, 2006. Addendum to Quality Assurance Project Plan for Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams: Addition of Skagit-Samish Watersheds, and Extension of Program through June 2009. Washington State Department of Ecology, Olympia, WA. Publication No. 03-03-104ADD. https://fortress.wa.gov/ecy/publications/summarypages/0303104add.html

Di Toro, D.M., H.E. Allen, H.L. Bergman, J.S. Meyer, P.R. Paquin, and R.C. Santore, 2001. Biotic Ligand Model of the Acute Toxicity of Metals: 1. Technical Basis. Environmental Toxicology and Chemistry 20(10): 2383-2396.

Dugger, D., P. Anderson, and C. Burke, 2007. Addendum to Quality Assurance Project Plan for Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams: Addition of Wenatchee and Entiat Watersheds in the Upper Columbia Basin. Washington State Department of Ecology, Olympia, WA. Publication No. 03-03-104ADD2. https://fortress.wa.gov/ecy/publications/summarypages/0303104add2.html

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

EPA, 1990. Specifications and Guidance for Obtaining Contaminate-Free Sample Containers. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Directive #9240.0-05.

EPA, 2007. Aquatic Life Ambient Freshwater Quality Criteria – Copper. U.S. Environmental Protection Agency, Office of Water. EPA-822-R-07-001. http://water.epa.gov/scitech/swguidance/standards/criteria/aqlife/copper/2007_index.cfm

Helsel, D.R., 2005. Nondetects and Data Analysis (NADA): Statistics for Censored Environmental Data. John Wiley & Sons, Inc., Publication, Hoboken, NJ.

Herrera Environmental Consultants, Inc., 2011. Toxics in Surface Runoff to Puget Sound: Phase 3 Data and Load Estimates. Washington State Department of Ecology, Olympia, WA. Publication No. 11-03-010. https://fortress.wa.gov/ecy/publications/summarypages/1103010.html

HydroQual, 2007. The Biotic Ligand Model Windows Interface, Version 2.2.3: User's Guide and Reference Manual, HydroQual, Inc, Mahwah, NJ. June 2007.

Johnson, A. and J. Cowles, 2003. Quality Assurance Project Plan: Washington State Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Habitat for Two Index Watersheds. Washington State Department of Ecology, Olympia, WA. Publication No. 03-03-104. https://fortress.wa.gov/ecy/publications/summarypages/0303104.html

Joy, J., 2006. Standard Operating Procedure (SOP) for Manually Obtaining Surface Water Samples, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP015. www.ecy.wa.gov/programs/eap/quality.html

Kittrell, F.W., 1969. A Practical Guide to Water Quality Studies of Streams. U.S. Department of the Interior/FWPCA. CWR-5. Washington, D.C. 135 pp.

Lemus, M.J. and K.S. Chung, 1999. Effect of Temperature on Copper Toxicity, Accumulation and Purification in Tropical Fish Juveniles Petenia Kraussii (Pisces: Cichlidae). Caribbean Journal of Science 35(1-2): 64-69.

McLain, K., 2013. Personal communication. Agency Scientist – Pesticides, Land Use, and Water Quality, Office of the Director – Natural Resource Assessment, Washington State Department of Agriculture, Olympia, WA.

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

Norton, D., D. Serdar, J. Colton, R. Jack, and D. Lester, 2011. Control of Toxic Chemicals in Puget Sound: Assessment of Selected Toxic Chemicals in the Puget Sound Basin, 2007-2011. Washington State Department of Ecology, Olympia, WA. Publication No. 11-03-055. https://fortress.wa.gov/ecy/publications/summarypages/1103055.html

Office of the Washington State Climatologist. Climate of Washington. http://www.climate.washington.edu/. Viewed July 25, 2013.

R Core Team, 2013. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. http://www.R-project.org/.

Sargeant, D., E. Newell, P.D. Anderson, and A. Cook, 2013. Surface Water Monitoring Program for Pesticides in Salmon-Bearing Streams, 2009-2011 Triennial Report. Washington State Department of Ecology, Olympia, WA. Publication No. 13-03-002. https://fortress.wa.gov/ecy/publications/summarypages/1303002.html

Shedd, J.R., 2011. Standard Operating Procedure (SOP) for Measuring and Calculating Stream Discharge, Version 1.1. Washington State Department of Ecology, Olympia, WA. SOP Number EAP056. www.ecy.wa.gov/programs/eap/quality.html

Swanson, T., 2007. Standard Operating Procedure (SOP) for Hydrolab® DataSonde® and MiniSonde® Multiprobes, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP033. www.ecy.wa.gov/programs/eap/quality.html

WAC 173-201A, 2006. Washington Administrative Code 173-201A. Water Quality Standards for Surface Waters of the State of Washington Chapter 173-201 WAC.

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

Whiley, A.J., 2011. Copper and Zinc Loading Associated with Automotive Brake-Pad and Tire Wear: Puget Sound Basin. Washington State Department of Ecology, Olympia, WA. Publication No. 11-10-087. https://fortress.wa.gov/ecy/publications/summarypages/1110087.html

Wood, C.M., H.A. Al-Reasi, and D.S. Smith, 2011. The Two Faces of DOC. Aquatic Toxicology 105(3-4): 3-8.

This page is purposely left blank

Appendices

This page is purposely left blank

Appendix A. Sampling Site Information

Table A-1. Locations and descriptions of sampling sites.

Site	Latitude	Longitude	Location Description
Green-Duwamish Watershed			
LC-1*	47.56252	122.36701	Approximately 4 meters upstream of the culvert under the 12th fairway on West Seattle Golf Course.
Skagit-Samish Watershed			
BD-1	48.30854	122.34744	Upstream side of the bridge on Milltown Road.
BS-1	48.34068	122.41394	Approximately 50 meters downstream of the tidegate at Fir Island Road.
IS-1	48.45059	122.46503	Approximately 57 meters East of Bayview-Edison Road on the upstream side of the tidegate and pump on Indian Slough.
SR-1*	48.52095	122.41131	Under bridge at Thomas Road crossing of the Samish River.
Lower Yakima Watershed			
MA-2*	46.33065	120.19999	Approximately 15 meters upstream of the Indian Church Road bridge over Marion Drain.
SP-3	46.23425	119.68540	Approximately 44 meters upstream of the culvert under West Hess Road; approximately 1.5 meters downstream of the Chandler Canal overpass of Spring Creek.
SU-1	46.251	120.0202	Downstream side of the bridge over Sulphur Creek Wasteway at Holaday Road and Midvale Road intersection; at USBR gauging station.
Wenatchee Watershed			
WE-1*	47.47238	120.37164	Upstream side of Sleepy Hollow Bridge near the center of the bridge.
MI-1	47.48743	120.48348	Upstream side of private bridge on Tripp Canyon Road.
PE-1	47.55726	120.58176	Approximately 50 meters downstream of bridge at Saunders Road.
BR-1	47.52103	120.48682	Approximately 40 meters upstream of the culvert under Evergreen Drive. Just downstream of a small wooden bridge.
Entiat Watershed			
EN-1	47.66318	120.25024	Approximately 25 meters downstream of private bridge at Keystone Road.

Datum: NAD83
*Biotic Ligand Model sampling locations.

Appendix B. Quality Assurance Data

Table B-1. Measure quality objectives.

Analysis	LCS (% recovery)	Duplicate (RPD)	Matrix Spike (% recovery)	Matrix Spike Duplicates (RPD)
Metals*	85-115	20	75-125	20
Hardness	85-115	20	75-125	20
Alkalinity	n/a	20	n/a	20
Chlorides	n/a	20	n/a	20
Sulfate	n/a	20	n/a	20

*Metals include: copper, calcium, magnesium, potassium, and sodium.

Table B-3. Transfer and filter blank results for copper (ug/L).

Date	Location	Parameter	Blank Type	Result	Qualifier
3/8/2012	MA-2	TR Cu	Transfer	0.1	U
3/8/2012	MA-2	Diss Cu	Filter	0.1	U
3/9/2012	LC-1	TR Cu	Transfer	0.12	
3/9/2012	LC-1	Diss Cu	Filter	0.1	U
5/15/2012	WE-1	TR Cu	Transfer	0.13	
5/15/2012	WE-1	Diss Cu	Filter	0.1	U
5/15/2012	BD-1	TR Cu	Transfer	0.1	U
5/15/2015	BD-1	Diss Cu	Filter	0.11	
7/25/2012	BR-1	TR Cu	Transfer	0.13	
7/25/2012	BR-1	Diss Cu	Filter	0.1	U
7/23/2012	IS-1	TR Cu	Transfer	0.11	
7/23/2012	IS-1	Diss Cu	Filter	0.18	
8/21/2012	EN-1	TR Cu	Transfer	0.22	
8/21/2012	EN-1	Diss Cu	Filter	0.1	U
8/22/2012	SU-1	TR Cu	Transfer	0.1	U
8/22/2012	SU-1	Diss Cu	Filter	0.1	U
8/20/2012	IS-1	TR Cu	Transfer	0.1	U
8/20/2012	IS-1	Diss Cu	Filter	0.1	U
8/20/2012	OC Wet Lab	TR Cu	Transfer	0.1	U
8/20/2012	OC Wet Lab	Diss Cu	Filter	0.1	U
8/20/2012	OC Wet Lab	TR Cu	Transfer	0.1	
8/20/2012	OC Wet Lab	Diss Cu	Filter	0.3	
9/5/2012	MI-1	TR Cu	Transfer	0.1	U
9/5/2012	MI-1	Diss Cu	Filter	0.48	
9/4/2012	SP-3	TR Cu	Transfer	0.1	U
9/4/2012	SP-3	Diss Cu	Filter	0.1	U
9/4/2012	LC-1	TR Cu	Transfer	0.52	

Diss: dissolved. OC: Operations Center. TR: total recoverable
U: The analyte was not detected at or above the reported sample quantitation limit.

Appendix C. Water Quality Criteria Data

Table C-1. Washington State water quality criteria for Longfellow Creek.

Date	Hardness (mg/L $CaCO_3$)	Dissolved Copper (ug/L)	Acute Criteria[1] (ug/L)	Chronic Criteria[2] (ug/L)
3/9/2012	139	1.20	23.21	15.04
3/23/2012	124	2.12	20.84	13.64
4/6/2012	130	1.96 J	21.79	14.20
4/17/2012	137	1.51 J	22.89	14.85
5/3/2012	92.6	2.55 J	15.83	10.63
5/15/2012	140	1.23 J	23.36	15.13
6/1/2012	105	2.54 J	17.82	11.83
6/15/2012	140	1.06 J	23.36	15.13
6/25/2012	123	1.60 J	20.68	13.55
7/13/2012	138	0.96 J	23.05	14.95
7/23/2012	130	1.15 J	21.79	14.20
8/10/2012	133	REJ	-	-
8/20/2012	135	0.95	22.58	14.67
9/4/2012	132	0.83	22.10	14.39

J: The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
REJ: The sample results are rejected.
[1] Acute copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.9422*[ln(hardness)]-1.464).
[2] Chronic copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.8545[ln(hardness)]-1.465).

Table C-2. Biotic Ligand Model (BLM) water quality criteria for Longfellow Creek.

Date	Dissolved Copper (ug/L)	Acute (ug/L)	Chronic (ug/L)
3/9/2012	1.20	23.25	14.44
4/6/2012	1.96 J	17.78	11.04
5/15/2012	1.23 J	23.1	14.35
6/1/2012	2.54 J	16.04	9.96
7/13/2012	0.96 J	11.37	7.07
8/10/2012	REJ	-	-
9/4/2012	0.83	12.71	7.89

REJ: The sample result is rejected.

Table C-3. Washington State water quality criteria for the Samish River.

Date	Hardness (mg/L $CaCO_3$)	Dissolved Copper (ug/L)	Acute Criteria[1] (ug/L)	Chronic Criteria[2] (ug/L)
3/9/2012	29.8	1.10	5.44	4.03
3/23/2012	31.5	0.93	5.73	4.23
4/6/2012	29.5	1.09 J	5.39	4.00
4/17/2012	27.0	1.54 J	4.96	3.71
5/4/2012	26.2	1.32 J	4.82	3.61
5/15/2012	34.3	0.90 J	6.21	4.55
6/1/2012	34.8	1.17 J	6.29	4.61
6/15/2012	39.5	0.87 J	7.09	5.13
6/25/2012	28.7	1.17 J	5.25	3.91
7/13/2012	40.1	0.86 UJ	-	-
7/23/2012	41.4	0.77 UJ	-	-
8/10/2012	50.4	0.68	8.92	6.32
8/20/2012	52.8	0.63	9.32	6.58
9/4/2012	54.8	0.63	9.65	6.79

J: The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

UJ: The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.

[1] Acute copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.9422*[ln(hardness)]-1.464).

[2] Chronic copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.8545[ln(hardness)]-1.465).

Table C-4. Biotic Ligand Model (BLM) water quality criteria for the Samish River.

Date	Dissolved Copper (ug/L)	Acute (ug/L)	Chronic (ug/L)
3/9/2012	1.10	11.74	7.29
4/6/2012	1.09 J	8.25	5.13
5/15/2012	0.90 J	5.80	3.60
6/1/2012	1.17 J	6.29	3.91
7/13/2012	0.86 UJ	-	-
8/10/2012	0.68	10.28	6.38
9/4/2012	0.63	9.37	5.82

Table C-5. Washington State water quality criteria for Brown Slough.

Date	Hardness (mg/L $CaCO_3$)	Dissolved Copper (ug/L)	Acute Criteria[1] (ug/L)	Chronic Criteria[2] (ug/L)
3/9/2012	902	0.70	4.80	3.10
3/23/2012	817	0.89	4.80	3.10
4/6/2012	940	0.64 J	4.80	3.10
4/17/2012	903	1.05 J	4.80	3.10
5/4/2012	474	0.52 UJ	-	-
5/15/2012	730	0.50 UJ	-	-
6/1/2012	660	1.06 J	4.80	3.10
6/15/2012	716	0.94 J	4.80	3.10
6/25/2012	280	1.00 U	4.80	3.10
7/13/2012	402	0.67 UJ	-	-
7/23/2012	402	0.53 UJ	-	-
8/10/2012	650	0.22	4.80	3.10
8/20/2012	226	0.76	4.80	3.10
9/4/2012	2510	**3.82**	4.80	3.10

bold: copper value above a copper criteria.
J: The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
U: The analyte was not detected at or above the reported sample quantitation limit.
UJ: The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.
[1] Acute marine standard based on a static value.
[2] Chronic marine standard based on a static value.

Table C-6. Washington State water quality criteria for Indian Slough.

Date	Hardness (mg/L $CaCO_3$)	Dissolved Copper (ug/L)	Acute Criteria[1] (ug/L)	Chronic Criteria[2] (ug/L)
3/9/2012	117	1.39	19.73	12.98
3/23/2012	102	2.01	17.34	11.54
4/6/2012	87.4	2.61 J	14.99	10.12
4/17/2012	70.7	2.35 J	12.27	8.44
5/4/2012	97.9	3.02 J	16.68	11.15
5/15/2012	112	0.83 J	18.93	12.51
6/1/2012	259	0.89 J	41.71	25.60
6/15/2012	176	0.62 J	28.99	18.40
6/25/2012	124	2.31 J	20.84	13.64
7/13/2012	130	0.68 UJ	-	-
7/23/2012	182	0.48 UJ	-	-
8/10/2012	387	0.61	60.90	36.08
8/20/2012	151	0.58	25.09	16.14
9/4/2012	191	0.83	31.31	19.73

J: The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

UJ: The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.

[1] Acute copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.9422*[ln(hardness)]-1.464).

[2] Chronic copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.8545[ln(hardness)]-1.465).

Table C-7. Washington State water quality criteria for downstream Big Ditch.

Date	Hardness (mg/L $CaCO_3$)	Dissolved Copper (ug/L)	Acute Criteria[1] (ug/L)	Chronic Criteria[2] (ug/L)
3/9/2012	187	2.44	30.69	19.38
3/23/2012	184	2.82	30.23	19.11
4/6/2012	188	2.74 J	30.84	19.47
4/17/2012	126	2.69 J	21.16	13.83
5/4/2012	110	5.57 J	18.62	12.31
5/15/2012	189	1.85 J	31.00	19.56
6/1/2012	166	2.26 J	27.43	17.50
6/15/2012	55.2	0.74 J	9.72	6.83
6/25/2012	140	2.32 J	23.36	15.13
7/13/2012	95.0	1.30 J	16.21	10.86
7/23/2012	63.7	1.10 J	11.13	7.72
8/10/2012	19.5	0.60	3.65	2.81
8/20/2012	23.6	0.63	4.37	3.31
9/4/2012	38.8	0.73	6.97	5.05

J: The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

[1] Acute copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.9422*[ln(hardness)]-1.464).

[2] Chronic copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.8545[ln(hardness)]-1.465).

Table C-8. Washington State water quality criteria for the Wenatchee River.

Date	Hardness (mg/L $CaCO_3$)	Dissolved Copper (ug/L)	Acute Criteria[1] (ug/L)	Chronic Criteria[2] (ug/L)
3/5/2012	35.4	0.39	6.40	4.67
3/21/2012	38.1	0.41	6.86	4.98
4/4/2012	44.0	0.55	7.85	5.63
4/17/2012	34.6	0.48	6.26	4.58
5/1/2012	20.5	0.41	3.82	2.93
5/15/2012	18.3	0.42	3.44	2.66
5/30/2012	15.1	0.42	2.87	2.26
6/11/2012	16.8	0.37	3.17	2.47
6/26/2012	13.3	0.33	2.54	2.02
7/10/2012	10.7	0.36	2.07	1.68
7/25/2012	15.3	0.33	2.90	2.28
8/6/2012	16.0	0.38	3.03	2.37
8/21/2012	20.1	0.35	3.75	2.88
9/5/2012	29.2	0.34 UJ	-	-

UJ: The analyte was not detected at or above the reported sample quantitation limit. The reported quantitation limit is approx. and may or may not represent the actual limit necessary to accurately measure the analyte in the sample.

[1] Acute copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.9422*[ln(hardness)]-1.464).

[2] Chronic copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.8545[ln(hardness)]-1.465).

Table C-9. Biotic Ligand Model (BLM) water quality criteria for the Wenatchee River.

Date	Dissolved Copper (ug/L)	Acute (ug/L)	Chronic (ug/L)
3/5/2012	0.39	12.81	7.96
4/4/2012	0.55	14.35	8.91
5/15/2012	0.42	5.43	3.37
5/30/2012	0.42	6.85	4.25
7/10/2012	0.36	4.59	2.85
8/6/2012	0.38	7.39	4.59
9/5/2012	0.34 UJ	-	-

Table C-10. Washington State water quality criteria for Peshastin Creek.

Date	Hardness (mg/L $CaCO_3$)	Dissolved Copper (ug/L)	Acute Criteria[1] (ug/L)	Chronic Criteria[2] (ug/L)
3/5/2012	95.6	0.41	16.31	10.92
3/21/2012	101 J	0.39	17.18	11.45
4/4/2012	101	0.62	17.18	11.45
4/17/2012	80.8	0.55	13.92	9.46
5/1/2012	60.9	0.49	10.66	7.43
5/15/2012	47.2	0.39	8.39	5.98
5/30/2012	46.6	0.32	8.29	5.91
6/11/2012	46.9	0.32	8.34	5.94
6/26/2012	41.1	0.32	7.36	5.31
7/10/2012	34.4	0.33	6.23	4.56
7/25/2012	46.3	0.28	8.24	5.88
8/6/2012	50.9	0.40	9.01	6.37
8/21/2012	51.4	0.32	9.09	6.43
9/5/2012	57.1	0.34 UJ	-	-

UJ: The analyte was not detected at or above the reported sample quantitation limit. The reported quantitation limit is approx. and may or may not represent the actual limit necessary to accurately measure the analyte in the sample.

[1] Acute copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.9422*[ln(hardness)]-1.464).

[2] Chronic copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.8545[ln(hardness)]-1.465).

Table C-11. Washington State water quality criteria for Brender Creek.

Date	Hardness (mg/L $CaCO_3$)	Dissolved Copper (ug/L)	Acute Criteria[1] (ug/L)	Chronic Criteria[2] (ug/L)
3/5/2012	189	0.64	31.00	19.56
3/21/2012	187	0.56	30.69	19.38
4/4/2012	174	1.25	28.68	18.22
4/17/2012	171	0.75	28.21	17.95
5/1/2012	85.1	0.59	14.62	9.89
5/15/2012	86.3	0.57	14.81	10.01
5/30/2012	76.0	0.73	13.14	8.98
6/11/2012	68.9	0.47	11.98	8.26
6/26/2012	65.4	0.52	11.41	7.90
7/10/2012	67.7	0.62	11.78	8.13
7/25/2012	85.5	0.54	14.68	9.93
8/6/2012	78.2	0.85	13.50	9.20
8/21/2012	78.9	1.39	13.61	9.27
9/5/2012	82.4	0.74 UJ	-	-

UJ: The analyte was not detected at or above the reported sample quantitation limit. The reported quantitation limit is approx. and may or may not represent the actual limit necessary to accurately measure the analyte in the sample.

[1] Acute copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.9422*[ln(hardness)]-1.464).

[2] Chronic copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.8545[ln(hardness)]-1.465).

Table C-12. Washington State water quality criteria for Mission Creek.

Date	Hardness (mg/L $CaCO_3$)	Dissolved Copper (ug/L)	Acute Criteria[1] (ug/L)	Chronic Criteria[2] (ug/L)
3/5/2012	123	0.55	20.68	13.55
3/21/2012	120	0.56	20.21	13.26
4/4/2012	114	0.70	19.25	12.70
4/17/2012	98.9	0.73	16.84	11.24
5/1/2012	82.8	0.58	14.24	9.66
5/15/2012	74.1	0.54	12.83	8.79
5/30/2012	81.4	0.48	14.02	9.52
6/11/2012	83.4	0.46	14.34	9.72
6/26/2012	89.3	0.40	15.30	10.30
7/10/2012	95.7	0.46	16.33	10.93
7/25/2012	100	0.47	17.02	11.35
8/6/2012	101	0.45	17.18	11.45
8/21/2012	108	0.43	18.30	12.12
9/5/2012	113	0.10 UJ	-	-

UJ: The analyte was not detected at or above the reported sample quantitation limit. The reported quantitation limit is approx. and may or may not represent the actual limit necessary to accurately measure the analyte in the sample.

[1] Acute copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.9422*[ln(hardness)]-1.464).

[2] Chronic copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.8545[ln(hardness)]-1.465).

Table C-13. Washington State water quality criteria for the Entiat River.

Date	Hardness (mg/L $CaCO_3$)	Dissolved Copper (ug/L)	Acute Criteria[1] (ug/L)	Chronic Criteria[2] (ug/L)
3/5/2012	48.3	0.23	8.57	6.09
3/21/2012	49.8	0.19	8.82	6.26
4/4/2012	52.2	0.26	9.22	6.51
4/17/2012	44.1	0.25	7.87	5.64
5/1/2012	22.4	0.24	4.16	3.16
5/15/2012	15.8	0.23	2.99	2.35
5/30/2012	15.0	0.21	2.85	2.24
6/11/2012	16.0	0.15	3.03	2.37
6/26/2012	13.1	0.16	2.51	2.00
7/10/2012	12.0	0.17	2.31	1.85
7/25/2012	18.8	0.17	3.52	2.72
8/6/2012	20.3	0.18	3.79	2.91
8/21/2012	25.2	0.19	4.64	3.50
9/5/2012	32.9	0.20 UJ	-	-

UJ: The analyte was not detected at or above the reported sample quantitation limit. The reported quantitation limit is approx. and may or may not represent the actual limit necessary to accurately measure the analyte in the sample.

[1] Acute copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.9422*[ln(hardness)]-1.464).

[2] Chronic copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.8545[ln(hardness)]-1.465).

Table C-14. Washington State water quality criteria for Marion Drain.

Date	Hardness (mg/L $CaCO_3$)	Dissolved Copper (ug/L)	Acute Criteria[1] (ug/L)	Chronic Criteria[2] (ug/L)
3/8/2012	143 J	0.69	23.84	15.41
3/20/2012	141	0.72	23.52	15.22
4/2/2012	94.6	0.97	16.15	10.83
4/18/2012	80.5	0.69	13.87	9.43
5/2/2012	82.0	0.80	14.11	9.58
5/16/2012	88.6	0.74	15.18	10.24
5/29/2012	76.2	0.71	13.17	9.00
6/12/2012	78.4	0.71	13.53	9.22
6/25/2012	74.1	0.73	12.83	8.79
7/9/2012	102	0.95	17.34	11.54
7/24/2012	94.3	2.04	16.10	10.80
8/8/2012	108	1.00	18.30	12.12
8/22/2012	90.6	0.81	15.50	10.43
9/4/2012	113	0.90	19.09	12.60

J: The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

[1] Acute copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.9422*[ln(hardness)]-1.464).

[2] Chronic copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.8545[ln(hardness)]-1.465).

Table C-15. Biotic Ligand Model (BLM) water quality criteria for Marion Drain.

Date	Dissolved Copper (ug/L)	Acute (ug/L)	Chronic (ug/L)
3/8/2012	0.69	27.17	16.88
4/2/2012	0.97	13.42	8.34
5/16/2012	0.74	13.98	8.68
5/29/2012	0.71	7.99	4.97
7/9/2012	0.95	8.78	5.45
8/8/2012	1.00	15.62	9.70
9/4/2012	0.90	16.89	10.49

Table C-16. Washington State water quality criteria for Sulphur Creek Wasteway.

Date	Hardness (mg/L $CaCO_3$)	Dissolved Copper (ug/L)	Acute Criteria[1] (ug/L)	Chronic Criteria[2] (ug/L)
3/6/2012	296	1.11	47.31	28.69
3/20/2012	95.9	0.78	16.36	10.95
4/2/2012	93.5	0.86	15.97	10.72
4/18/2012	106	0.79	17.98	11.93
5/2/2012	109	0.86	18.46	12.22
5/16/2012	113	0.96	19.09	12.60
5/29/2012	84.0	0.80	14.44	9.78
6/12/2012	103	0.86	17.50	11.64
6/25/2012	73.7	0.77	12.76	8.75
7/9/2012	101	0.99	17.18	11.45
7/24/2012	99.0	0.99	16.86	11.25
8/8/2012	103	0.96	17.50	11.64
8/22/2012	110	0.90	18.62	12.31
9/4/2012	128	1.09	21.47	14.02

[1] Acute copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.9422*[ln(hardness)]-1.464).
[2] Chronic copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.8545[ln(hardness)]-1.465).

Table C-17. Washington State water quality criteria for Spring Creek.

Date	Hardness (mg/L $CaCO_3$)	Dissolved Copper (ug/L)	Acute Criteria[1] (ug/L)	Chronic Criteria[2] (ug/L)
3/6/2012	283	0.79	45.35	27.61
3/20/2012	265	0.86	42.62	26.10
4/2/2012	99.1	0.93	16.87	11.26
4/18/2012	182	1.09	29.92	18.93
5/2/2012	74.3	0.91	12.86	8.81
5/16/2012	205	1.16	33.47	20.96
5/29/2012	60.9	0.80	10.66	7.43
6/12/2012	125	1.08	21.00	13.74
6/25/2012	54.8	0.74	9.65	6.79
7/9/2012	71.1	0.85	12.34	8.48
7/24/2012	135	1.03	22.58	14.67
8/8/2012	129	1.27	21.63	14.11
8/22/2012	103	1.12	17.50	11.64
9/4/2012	150	1.40	24.93	16.05

[1] Acute copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.9422*[ln(hardness)]-1.464).
[2] Chronic copper criteria are derived from the following hardness-based equation: (0.960)*e^(0.8545[ln(hardness)]-1.465).

Appendix D. Glossary, Acronyms, and Abbreviations

Glossary

Complexation: The forming of molecular entities by loose association.

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 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.

Salmonid: Fish that belong to the family *Salmonidae*. Species of salmon, trout, or char. www.fws.gov/le/ImpExp/FactSheetSalmonids.htm

Speciation: The chemical form or compound in which an element occurs in both non-living and living systems.

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.

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.

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

Acronyms and Abbreviations

BLM	Biotic Ligand Model
DOC	Dissolved Organic Carbon
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
LCS	Laboratory Control Standard
MEL	Manchester Environmental Laboratory
MS/MSD	Matrix Spike/Matrix Spike Duplicate
MQO	Measurement Quality Objective
QA	Quality Assurance
QC	Quality Control
SOP	Standard Operating Procedures
USGS	U.S. Geological Survey
WAC	Washington Administrative Code
WSDA	Washington State Department of Ecology

Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
lbs/day	pounds per day
mg/L	milligrams per liter (parts per million)
ppm	parts per million
s.u.	standard units
ug/L	micrograms per liter (parts per billion)
um	micrometer