Technical Support Document:
An Evaluation to Derive Statewide Copper Criteria Using the Biotic Ligand Model

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About This Document

This document contains results and conclusions from a statewide analysis of data needed to support development of potential statewide freshwater aquatic life water quality criteria for copper using the Environmental Protection Agency's 2007 nationally recommended criteria for copper, which are based on the Biotic Ligand Model (BLM). DEQ anticipates the BLM copper criteria will replace EPA's 1985 copper criteria based on the hardness of water, which is currently in effect in Oregon. DEQ will use this document in agency and advisory committee discussions in preparation for rulemaking to revise the freshwater aquatic life water quality standard for copper in Oregon.

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Executive Summary

In 2015, the Oregon Department of Environmental Quality conducted an analysis of the copper Biotic Ligand Model in preparation for replacing the state's aquatic life water quality standard for copper based on water hardness with a statewide adoption of the BLM. DEQ conducted this analysis in response to EPA's 2013 disapproval of the copper criteria Oregon adopted in 2004. The disapproved criteria were EPA's 1995 nationally recommended dissolved copper criteria for freshwater, which are dependent on the hardness of water. The EPA 1995 copper standard is still in effect in most states. Given EPA's disapproval, Oregon's prior criteria, which are based on EPA's1985 recommendations remain in effect. In 2007, EPA updated its national recommendation for copper, which uses the BLM to derive freshwater aquatic life criteria. The BLM requires 11 input parameters to derive criteria based on site-specific water chemistry. In its action letter, EPA indicated that state adoption of the BLM would remedy their disapproval action.

An external technical review panel reviewed this Technical Support Document during several phases of analysis and provided input to DEQ. DEQ incorporated this feedback throughout the document. A summary of reviewer input that focused on a number of broad analytical questions is in section X.

This evaluation was based on a dataset of over 22,000 samples with complete or near complete BLM datasets gleaned over 15 years from 306 U.S. Geological Survey and 517 Oregon DEQ water quality monitoring stations across the state.

Because of the number of model input parameters, a major objective of this analysis was to evaluate methods to estimate values for missing model inputs. A valid method for estimating geochemical ion concentrations using specific conductance measurements is in section VI.A. DEQ also presents an approach in section VI.B to simplify large geographic scales by combining EPA Level-III Ecoregions into four physiographic BLM assessment regions for evaluating potential regional estimates of BLM parameters or criteria where model data are insufficient or absent.

The BLM copper criteria will be used in Clean Water Act programs, such as National Pollutant Discharge Elimination System (NPDES) permitting and water quality assessment. Therefore, DEQ compared the currently effective hardness-based criteria from EPA 1985 recommendations to BLM criteria to learn about t relationship and whether that relationship varies by geographic area or water chemistry. Based on the valid assumption that BLM criteria are more accurate than hardness-based criteria this analysis also shows where hardness-based criteria may be higher or lower than BLM criteria, which would lead to under-protection or over-protection, respectively, of aquatic life.

Section V of this document examines the range and characteristics of available BLM data. This data was used to: (1) examine the time-variability of BLM criteria; (2) determine where dissolved copper concentrations currently exceed BLM criteria; and (3) evaluate methods to develop BLM criteria for locations where site-specific data are insufficient. One method is to estimate missing input parameters based on which physiographic region the site is located in. The other method explored the possibility of developing estimated BLM criteria based on physiographic regions to apply at sites with insufficient data.

DEQ also contrasted the effect of using data from Oregon with the EPA proposed method to estimate dissolved organic carbon. DOC is a very sensitive parameter in the BLM and DOC data is not widely available. DEQ also examined one method for determining the minimum number of samples needed to ensure development of protective criteria. In addition, DEQ explored BLM datasets to determine where data may be sufficient to use the Fixed Monitoring Benchmark. The FMB procedure establishes single acute and chronic benchmark values that take into account time varying BLM criteria results and an allowed exceedance frequency (e.g. not to exceed more than once every three years). The FMB approach was developed in context with BLM evaluations in Colorado, but this approach could apply to any water quality criteria that depend on water chemistry, such as ammonia or hardness-based metals.

This technical analysis serves as the scientific basis for developing rulemaking options for the advisory committee, which is expected to meet four times from December 2015 to April 2016. The committee will provide input on key implementation questions, including how to adopt BLM copper criteria into the Oregon Administrative Rules. DEQ expects to recommend revisions to the state's current aquatic life copper criteria in Table 30 (OAR-40-041-8033) to the Environmental Quality Commission in December 2016.

Summary of Results

- DEQ developed a large database to calculate BLM criteria. DEQ compiled data from the DEQ LASAR database and the USGS database at 823 locations around the state.
- There were a limited number of locations and sampling events that had measured data for all of the required BLM input parameters coincidently. Therefore, to derive BLM criteria, estimating some missing parameters will frequently be required.
- The outcome of DEQ's analysis verified that the BLM criteria calculations are most sensitive to DOC and pH. Consequently, estimating values for DOC or pH results in significant uncertainty in the accuracy of BLM criteria. DEQ's analysis indicates there are no routinely collected surrogate parameters that can be used to accurately estimate DOC or pH.
- A strong relationship can sometimes be found between alkalinity, pH and inorganic carbon in chemical datasets. In its dataset, DEQ did not find an empirical relationship that could be used to predict pH from ambient alkalinity measures.
- Temperature is a required BLM input parameter. Because temperature data is extensively collected throughout Oregon, DEQ could not identify a commonly collected surrogate for estimating temperature at a site and did not investigate whether any other surrogate could be used to estimate temperature when data are missing. Further, DEQ's analysis suggests that the model, as applied in Oregon, is not strongly sensitive to temperature.
- Measurements of specific conductance were found to provide strong correlations (high $R^2$of 0.819 – 0.973) to geochemical ions and alkalinity concentrations across the entire BLM dataset. Thus, specific conductance provides a strong surrogate for estimating the concentration of these parameters when data are missing.
- By using specific conductance data to estimate missing geochemical and alkalinity parameters, there were sufficient data to calculate BLM criteria for 4,607 sample sets from 469 individual sites distributed across the state.

- BLM criteria were generally higher than Oregon's currently effective hardness-based criteria, which are based on EPA's 1985 total recoverable copper criteria recommendations. Out of 342 samples with complete measured BLM parameters and paired hardness data, approximately 52 percent of samples had higher hardness-based criteria than BLM criteria. The remaining 48 percent of these samples, where hardness-based criteria were lower than the BLM criteria, more frequently occurred at sites in the North Coast and Willamette Valley.
- Relatively low BLM criteria were attributable to very low DOC (less than 1.5 milligrams per liter) and lower pH (less than 7.4) conditions. This indicates that the existing hardness-based criteria may not be adequately protective of aquatic life under similar conditions of water chemistry.
- Using regionally aggregated observations of DOC from either EPA's Level-III Ecoregions or DEQ's proposed BLM physiographic regions provides a conservative method for estimating copper criteria where site-specific DOC data are insufficient. The choice of the statistic to use as an estimate for DOC, given the range of DOC values within a geographic region, has a significant bearing on the BLM outcome.
- The EPA's recommended 10^{th} percentile values for DOC produced the most conservative BLM criteria estimates compared to 10^{th} percentile or median estimates using DEQ data, or median estimates using EPA data.
- The similarity between EPA's recommended 10^{th} percentile data and DEQ's estimated 10^{th} percentile data provides strong evidence that DEQ may reliably derive estimates for parameters from its own database.
- Both the median and 10^{th} percentile of all the BLM criteria generated by the Oregon dataset are near or below the quantification limit (QL) of 1.5 micrograms per liter frequently reported for copper in the existing data set.
- There are temporal patterns in the variability of DOC and pH that may affect the long-term protectiveness of any single BLM criterion generated for a particular site. Understanding the temporal variation in these parameters is important when determining how to apply the criteria appropriately.
- For sites where DEQ had sufficient measured data to derive BLM criteria, the number of samples where dissolved copper concentrations exceed chronic BLM criteria is 2 percent statewide. The rate is higher for samples in the Willamette Valley (2.7 percent) and Cascades (7.3 percent).
- At least 12 consecutive monthly samples may be necessary to accurately characterize the temporal variability at a given location for application of a Fixed Monitoring Benchmark approach.

I. Introduction

In January 2013, the Environmental Protection Agency (EPA) disapproved[1] Oregon's revised freshwater copper standard that DEQ submitted for approval in 2004 on the basis that it was inconsistent with the EPA national criteria for copper. The copper criteria that DEQ adopted in 2004 was based on water hardness following EPA's 1995 304(a) recommendations, while EPA's latest 2007 recommendations for copper are based on the Biotic Ligand Model.

As part of Endangered Species Act consultation requirements, the National Marine Fisheries Service's biological opinion[2,3] completed on August 14, 2012 concluded the proposed copper criteria would cause jeopardy to a number of threatened or endangered species[4]. Both agencies concluded that copper criteria based on the Biotic Ligand Model would be sufficiently protective. Criteria developed using the BLM are based on a model which generates criteria that vary depending on the water chemistry in each monitoring sample.

This model requires eleven different water quality parameters (including calcium and magnesium, which determine hardness) collected at specific water body locations to derive site-specific criteria (see **Table 1**). These parameters influence the bioavailability of copper, and thus toxicity, to sensitive aquatic species. EPA's 2007 criteria document provides a number of studies (Playle et al., 1992, 1993a,b; Janes and Playle, 1995; MacRae et al., 1999; Meyer et al.,1999, 2002; McGeer et al., 2002) that examine the relationship of complexing ligands and competing cations and copper toxicity. The BLM provides a more accurate prediction of toxic copper concentrations than those provided by water hardness alone. Copper criteria derived using the BLM may result in criteria that may be either higher or lower than the criteria based on hardness that are currently in effect.

Table 1: Eleven model parameters for the copper BLM:

- temperature
- pH
- dissolved Organic Carbon (DOC)
- calcium (Ca) $^{2+}$
- magnesium (Mg) $^{2+}$
- sodium (Na) $^{1+}$
- potassium (K) $^{1+}$
- sulfate (SO_4) $^{2-}$
- chloride (Cl) $^{1-}$
- alkalinity
- humic acid

[1] See EPA action documents at: http://www.deq.state.or.us/wq/standards/toxicsEPAaction.htm.

[2] National Marine Fisheries Service. Jeopardy and Destruction or Adverse Modification of Critical Habitat Endangered Species Act Biological Opinion for Environmental Protection Agency's Proposed Approval of Certain Oregon Administrative Rules Related to Revised Water Quality Criteria for Toxic Pollutants. NMFS Consultation Number: 2008/00148. August 14, 2012. The jeopardy decision also included acute and chronic freshwater criteria for ammonia and aluminum, and the freshwater acute criterion for cadmium.

[3] The U.S. Fish and Wildlife Service, in their July 30, 2012 Biological Opinion, did not find jeopardy with Oregon's toxics criteria, including copper. The USFWS's jurisdiction includes protecting threatened and endangered freshwater aquatic species such as mollusks, Bull Trout, Oregon Chub, Lost River and Shortnose Suckers.

[4] Includes LCR Chinook salmon, UWR Chinook salmon, UCR spring-run Chinook salmon, SR spring/summer-run Chinook salmon, SR fall-run Chinook salmon, CR chum salmon, LCR coho salmon, SONCC coho salmon, OC coho salmon, SR sockeye salmon, LCR steelhead, UWR steelhead, MCR steelhead, UCR steelhead, SRB steelhead, green sturgeon, eulachon (anadromous smelt), Southern Resident killer whales.

DEQ is evaluating how the Biotic Ligand Model could be applied statewide to replace Oregon's hardness-based copper criteria in response to EPA's disapproval. EPA's action letter indicated that Oregon could develop BLM copper criteria where data are sufficient, or Oregon could establish default BLM criteria applied on a statewide or regional basis. The resulting criteria would need to incorporate sufficient data to account for temporal and spatial variability to ensure that the derived criteria are protective of designated uses. Alternatively, to address NMFS's concern about Oregon's 2004-adopted criteria, Oregon could either re-submit the criteria with additional scientific justification, or develop revised hardness-based criteria, so that it is protective of aquatic life uses.

The Environmental Quality Commission must adopt and EPA Region 10 must approve any revised copper aquatic life criteria, including criteria based on the BLM, before the criteria are effective for Clean Water Act purposes. Oregon will initiate further discussions with EPA and the rulemaking advisory committee about how EPA's approval process could be streamlined through a performance-based standard approach where EPA would not need to approve each BLM criterion.

I.A. Purpose of Document

Like hardness-based criteria, the Biotic Ligand Model is intended to be applied at a specific location based on site-specific water chemistry. A number of states[5] have used the BLM or have modified the copper hardness-based equation using a Water Effects Ratio as alternatives to hardness-based criteria, yet states have still retained the hardness-based criteria in their water quality standards regulations. Because adequate BLM input data may not be sufficient throughout the state, EPA's 2007 copper criteria implementation documents suggest alternatives to statewide BLM adoption through an incremental or targeted application of the BLM, while retaining hardness-based criteria. However, an incremental adoption of the BLM in Oregon may not be possible in light of EPA disapproval of its hardness-based criteria and the NMFS's jeopardy decision. Therefore, Oregon initiated this study in part to evaluate methods to determine how to adopt the BLM statewide when adequate data were not available.

In addition, DEQ may develop a BLM procedures document following the adoption of this rule. This document would provide procedures and instructions to DEQ staff in developing BLM criteria or evaluating BLM criteria requested by third parties for specific waterbodies. Rulemaking may also require DEQ to develop a procedures document to be adopted by reference into the administrative rules that specifies estimation methods to be used when BLM input data are not available. Although DEQ developed the analyses in this document for purposes of evaluating the use of the BLM statewide, these analyses are not final. Methods, such as estimation of geochemical ions using specific conductance, are subject to further analyses if updated information becomes available. DEQ will use the results and information contained in this analysis for developing rulemaking options to the advisory committee, as well as developing any procedure documents.

[5] States, such as Colorado, Georgia, Kansas, Maine, Michigan, and Iowa are developing site-specific criteria using the BLM. Kansas, Delaware and Idaho are proposing to replace their hardness-based criteria with the BLM. As of Nov. 30, 2015, EPA had not yet approved criteria revisions in Kansas or Delaware. Idaho's rulemaking is still in progress.

Below are questions DEQ explored in developing this document:

- What is the availability of BLM data statewide?
- Based on an Oregon dataset, which BLM parameters are the most sensitive for calculating copper toxicity?
- Are there valid methods to estimate missing BLM parameters?
- Does the addition of stream order improve the ability to estimate missing BLM parameters?
- If using estimated BLM criteria or parameters and various statistical applications, what would BLM default criteria look like?
- How does DEQ's proposed approach for estimating DOC for deriving BLM criteria compare to EPA's DOC estimation approach?
- Because much of the existing BLM data in Oregon are expressed as total recoverable, would using total recoverable data in place of dissolved data significantly influence criteria derivation results?
- How do hardness-based criteria compare to BLM criteria statewide?
- How do hardness-based criteria versus BLM criteria vary over time given varying water quality characteristics?
- For waterbody locations with copper data, where would exceedances of BLM criteria be expected? Are there exceedance patterns based on geographic regions?
- Are there sufficient BLM data in Oregon to support development of BLM Fixed Monitoring Benchmarks (FMB)? Is there a minimum sample size needed to develop copper FMBs and could this same minimum sample size apply in developing BLM copper criteria using Instantaneous Water Quality Criteria?

I.B. Technical Review Panel

To evaluate the analyses contained in this document, DEQ selected a technical review panel (**Table 2**) whose members have knowledge and expertise in using this model, are metal, geochemical or water quality standards experts, or have an aquatic toxicity or ecological risk background. This document will be part of the rulemaking record. DEQ will summarize the technical review panel's conclusions, and where possible, summarize panel member agreement or disagreement and significant issues raised. The technical review panel is not a decision-making body, but rather, it will provide technical review and input on DEQ's analyses.

Table 2: Technical Review Panel			
Member	**Affiliation**	**Contact Information**	**Area of Expertise**
1. Kathleen Collins	EPA, Region 10	collins.kathleen@epa.gov 206-553-2108	water quality standards
2. Luis Cruz, Joe Beaman	EPA, Headquarters	cruz.luis@epa.gov 202-566-1095 beaman.joe@epa.gov 703-347-0317	water quality standards, aquatic toxicology, ecological risk
3. Jeff Lockwood	National Marine Fisheries Service, NOAA	jeffrey.lockwood@noaa.gov 503-231-2249	ecological risk/Endangered Species Act
4. Chris Mebane	USGS	cmebane@usgs.gov 208-387-1308	aquatic toxicology, ecological risk, BLM user
5. Dianne Barton	Columbia River Intertribal Fish Commission	bard@critfc.org 503-731-1259	aquatic toxicology, ecological risk
6. Dr. William Stubblefield	Oregon State University	Bill.Stubblefield@oregonstate.edu 541-737-2565	metals, aquatic toxicology, ecological risk, BLM user
7. Dr. Jeff Louch, Dr. Barry Malmberg	National Council for Air and Stream Improvement, Inc.	jlouch@ncasi.org 541-752-8801 bmalmberg@ncasi.org 541-752-8801, x317	water quality standards
8. Robert Baumgartner	Clean Water Services	BaumgartnerB@CleanWaterServices.org 503-681-4464	water quality standards, BLM user
9. Dr. Robert Gensemer, Carrie Claytor, John Gondek, Amanda Kovach	GEI Consultants	bgensemer@geiconsultants.com 303-476-1772	metals, water quality standards, ecological risk, BLM user, site-specific and statewide standards updates
10. Scott Tobiason, Robert Santore, Dave DeForest	Windward Environmental, LLC	ScottT@windwardenv.com 206-812-5424	metals, water quality standards, ecological risk, BLM user, site-specific and statewide standards updates

I.C. Objectives

Because of the large data requirements of the model, one of DEQ's objectives was to evaluate whether commonly collected field water quality parameters, such as specific conductance, could be used to estimate missing model parameters that require lab analysis. If so, the number of parameters requiring lab analysis could be reduced to save time and expense. This approach could also be helpful for derivation of criteria based on existing partial BLM datasets. Another objective of this analysis was to identify the most sensitive model parameters based on the ranges found in the Oregon dataset. This sensitivity analysis would establish which parameters are most important to collect, and which parameters could be estimated because they are not as sensitive.

Another objective was to evaluate whether DEQ could establish default BLM criteria values or default model parameters when missing based on certain physiographic regions. A physiographic region delineates areas of the state with similar water chemistry characteristics. If so, BLM default criteria or parameters could apply to waterbody segments within a physiographic region when model data are insufficient to derive criteria at a certain site.

In addition, DEQ sought to compare hardness-based criteria with BLM-derived criteria in an effort to understand the locations and conditions where hardness-based criteria are currently higher or lower when compared to BLM criteria. Identifying these locations may be used to prioritize where additional BLM data should be collected.

Specific analyses include:

1. Description of DEQ's data sources, state coverage and quality assurance
2. Rationale for using total data when dissolved data for BLM input parameters are absent
3. Sensitivity of model parameters based on Oregon data
4. Methodology to estimate missing BLM parameters using specific conductance
5. Methodology to delineate potential BLM georegions
6. General statewide comparison showing where hardness-based criteria are under- or over-protective when compared to BLM criteria

II. Aquatic Life Effects, Sources, and Presence of Copper

II.A. Effects to Freshwater Aquatic Life and Sources

Copper is a naturally occurring metal found in the earth's crust. At low concentrations, copper is an essential element to plants, animals and humans; however, at higher concentrations copper can be toxic to aquatic life, such as fish, amphibians and invertebrates. For example, fish gills can become damaged and lose their ability to osmoregulate ions, such as sodium and chloride. These ions are important for the normal functioning of the cardiovascular and nervous systems. Other effects include reduced growth and survival rates and reproductive effects.[6] Among Pacific salmon, some research shows that copper can affect olfaction (sense of smell) [7]. Fish rely on their sense of smell to find food, avoid predators and migrate. Although BLM versions 2.2.3 and 2.2.4 do not include toxicity studies with salmonid olfactory endpoints, some studies show that BLM criteria would nonetheless protect against olfactory effects on salmonids.[8,9] For a summary of additional toxic effects of copper to aquatic life, see the National Marine Fisheries Service's biological opinion.[10]

Copper can be released into the environment through a wide variety of sources including:

- manufacturing (e.g. brake pads, fabricated metal products, electrical equipment);
- wastewater discharges from corrosion of copper pipes and industrial discharges;
- industrial, commercial, highway and general urban storm water runoff;
- agricultural or residential use of pesticides containing copper (e.g. copper sulfate);
- marine anti-fouling paints;
- roofing materials;
- wood preservatives (e.g. copper azole);
- air emissions (e.g. gas and diesel combustion);
- soil erosion;
- mining; and
- natural weathering processes

[6] Eisler, Ronald. 2008. Copper Hazards to Fish, Wildlife and Invertebrates: A Synoptic Review. Biological Science Report. USGS/BRD/BSR--1997-0002.

[7] McIntyre, Jenifer K., David H. Baldwin, James P. Meador and Nathaniel L. Scholz (2008). Chemosensory Deprivation in Juvenile Coho Salmon Exposed to Dissolved Copper under Varying Water Chemistry Conditions. Environmental Science and Technology 42: 1352-1358.

[8] David K. DeForest, Robert W. Gensemer, Eric J. Van Genderen, and Joseph W. Gorsuch. Protectiveness of Water Quality Criteria for Copper in Western United States Waters Relative to Predictive Olfactory Responses in Juvenile Pacific Salmon. Integrated Environmental Assessment and Management. Volume 7, Number 3—pp. 336–347 © 2011 SETAC.

[9] Meyer JS, Adams WJ. 2010. Relationship Between Biotic Ligand Model-Based Water Quality Criteria and Avoidance and Olfactory Responses to Copper by Fish. Environ Toxicol Chem 29:2096-2103.

[10] National Marine Fisheries Service. Jeopardy and Destruction or Adverse Modification of Critical Habitat Endangered Species Act Biological Opinion for Environmental Protection Agency's Proposed Approval of Certain Oregon Administrative Rules Related to Revised Water Quality Criteria for Toxic Pollutants. NMFS Consultation Number: 2008/00148. August 14, 2012. The jeopardy decision also included acute and chronic freshwater criteria for ammonia and aluminum, and the freshwater acute criterion for cadmium. Pgs. 303-315.

II.B. Summary of Copper Presence in Oregon

The mean copper concentration[11] in Oregon surface waters (the majority are river samples) is 1.9 µg/L with a range of 0.02 – 64.3 µg/L. The median and range differs slightly whether considering the total recoverable or dissolved measurements of concentration (**Table 3**). There are approximately 21 industrial dischargers that have permit limits for total recoverable copper. Currently, there are no municipal dischargers exceeding copper permit limits based on the currently effective copper criteria. The industrial stormwater 1200Z permit includes a total recoverable copper benchmark of 20 µg/L.

Table 3: Summary of copper concentration in Oregon surface waters

Summary	Dissolved Cu (µg/L)	Total Recoverable Cu (µg/L)
median	1.21	1.70
min.	0.063	0.02
max	51.9	64.3
n=	1763	3935

The 2010 Integrated Report, which is Oregon's most current assessment, shows the number of waterbodies in the following listing categories based on the current total recoverable hardness based copper criteria:

Category 5 (impaired and TMDL needed): 14
Category 4 (impaired but TMDL not needed): 0
Category 3 (insufficient data): 106
Category 3B (potential concern): 26
Category 2 (attaining): 11

EPA has not yet approved Oregon's 2012 Integrated Report, but DEQ expects EPA to propose additional 303(d) listings for copper. If a waterbody is listed for a pollutant, a mixing zone is generally not allowed and the wastewater discharger, in many circumstances, must meet pollutant limits at the end of pipe (i.e., no dilution allowed). In addition, DEQ must develop a Total Maximum Daily Load for that waterbody. Currently, there are no TMDLs for copper in Oregon.

III. EPA Criteria Development

For the summary below, DEQ referenced information related to the acute and chronic development of copper criteria based on EPA's 2007 criteria document[12].

[11] This number represents both total and dissolved copper concentrations. At sites with both total and dissolved results, DEQ conservatively used total copper results for statistical analysis purposes. DEQ and USGS agencies identified these samples as "surface waters", although, some results may be affected by point or nonpoint sources. The maximum value of 64.3 ug/L is from a sample collected near the Hawthorne Bridge on the Willamette River in downtown Portland, Oregon.

[12] EPA. *Aquatic Life Ambient Freshwater Quality Criteria – Copper*. 2007 Revision. Office of Water. EPA-822-R-07-001.

EPA reviewed approximately 350 studies to derive its national recommendation for acute criteria. Toxicity endpoints for development of the acute criteria are mortality and immobilization. There were 27 genera representing 15 species of invertebrates, 22 species of fish and one amphibian species. Nine of the ten most sensitive genera were invertebrates. The most sensitive invertebrate genera were *Daphnia*. The salmonid genus *Oncorhynchus* was the most sensitive fish genus and ranked number ten.

The toxicity endpoints for development of the chronic criteria include survival, growth and reproductive effects. Because there was insufficient data to develop chronic criteria as specified in EPA guidance[13], EPA used the acute to chronic ratio methodology to derive copper chronic criteria.

In order for EPA to derive copper criteria using the BLM, EPA had to identify applicable toxicity tests where the BLM input parameters were available, or could be estimated[14]. EPA then normalized all of the toxicity data to common water chemistry conditions, so that the sensitivities of aquatic genera could be ranked in support of criteria development. Any default water chemistry could have been used for this purpose. EPA chose a moderately hard, reconstituted water, as defined below:

- temperature = 20^{o}C
- pH = 7.5
- Dissolved Organic Carbon (DOC) = 0.5 mg/L
- calcium (Ca) = 14.0 mg/L
- magnesium (Mg) = 12.1 mg/L
- sodium (Na) = 26.3 mg/L
- potassium (K) = 2.1 mg/L
- sulfate (SO_4) =81.4 mg/L
- chloride (Cl) = 1.90 mg/L
- alkalinity = 65.0 mg/L
- sulfide (S) = 0.0003 mg/L

Using these parameters for BLM input result in 2.3 µg/L for the acute criterion, and 1.5 µg/L for the chronic criterion in a low DOC water representative of the synthetic samples used in laboratory toxicity test conditions. In their biological opinion, NMFS staff indicated that these BLM criteria concentrations satisfy the conservation needs of threatened and endangered species and their critical habitat. EPA discussions with NMFS indicate that if sufficient data exist to derive alternate BLM criteria values based on Oregon-specific data, that these criteria would also be protective of threatened and endangered species. Oregon stream chemistry can vary considerably, most notably DOC, from the moderately hard BLM

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[13] Stephan, C.E., D.I. Mount, D.J. Hansen, J.H. Gentile, G.A. Chapman, and W.A. Brungs, 1985. *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses*. PB85-227049. National Technical Information Service, Springfield, Virginia. EPA.

[14] EPA. 2003 *Draft Update of Ambient Water Quality Criteria for Copper*. U. S. Environmental Protection Agency, EPA 822-R-03-026, November 2003.

input parameters EPA used to derive the criteria. Because DOC is one of the BLM parameters with the strongest influence on copper bioavailability, DEQ would expect BLM criteria in Oregon to be different from the criteria suggested by NMFS.

IV. Model Description and Background

IV.A Biotic Ligand Model Description

The Biotic Ligand Model is a product of almost 15 years of development[15,16] incorporating decades of copper toxicity research, and is EPA's currently recommended methodology to derive freshwater copper criteria. Therefore, this document does not intend to evaluate the basis of the model and its underlying models, or aquatic life protectiveness. However, some basic principles of the model are described below. DEQ referenced most of the following information from EPA's technical support document[17].

The BLM is a mechanistic model, which predicts the accumulation of copper[18] at a biotic ligand at or above a critical threshold that leads to acute toxicity. Copper toxicity results primarily from the cupric ion, Cu^{2+}, and to a lesser extent copper monohydroxide, $CuOH^{+}$. A "ligand" is an ion, molecule, or molecular group that binds to a metal to form a larger complex. A "biotic ligand" is a ligand except that the biochemical receptor is on an organism, such as a fish gill. The metal accumulation on a biotic ligand is termed the LA50, or the Lethal Accumulation that results in 50% mortality to exposed organisms.

Since the BLM accounts for inorganic and organic copper speciation and competitive complexation with the biotic ligand, the amount of copper that accumulates at that site will vary depending on site-specific water chemistry (see **Figure 1** below). Summarizing this concept leads to the "three C's" that drive copper toxicity: (1) **C**oncentration of copper; (2) **C**omplexation of copper; and (3) **C**ompetition of copper with cations at the site of toxicity. Therefore, applying these principles, the model predicts the concentration of copper in water that would result in acute toxicity to aquatic species. The eleven BLM water chemistry parameters include: (1) temperature; (2) pH; (3) DOC; (4) Ca^{2+}; (5) Mg^{2+}; (6) Na^{+}; (7) K^{+}; (8) SO_4^{2-}; (9) Cl^{-}; (10) alkalinity and (11) humic acid. Several other input parameters are calculated values. Dissolved organic carbon commonly originates from decaying natural organic matter (NOM).

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

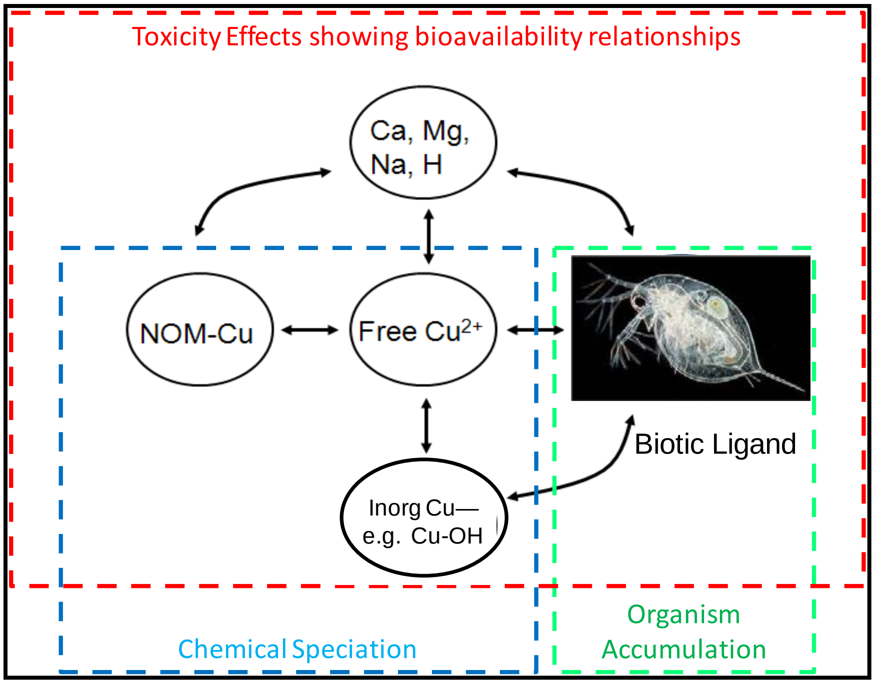
[16] Santore, R.C., D.M. DiToro, P.R. Paquin, and J.S. Meyer, 2001. A Biotic Ligand Model of the Acute Toxicity of Metals. II. Application to Acute Copper Toxicity in Freshwater Fish and Daphnia. Environmental Toxicology and Chemistry 20(10):2397-2402.

[17] EPA 2007. Office of Science and Technology, Health and Ecological Criteria Division. Washington D.C. The Biotic Ligand Model: Technical Support Document for Its Application to the Evaluation of Water Quality Criteria for Copper. Undated.

[18] A BLM has also been developed for other metals, such as silver, cadmium and zinc.

Hardness-based copper criteria do not explicitly consider the effects of DOC and pH, two of the more important parameters affecting copper bioavailability and thus toxicity. Not considering these and other chemical parameters results in copper criteria that are potentially under-protective at low pH and DOC and potentially over-protective at higher DOC levels as compared to BLM criteria. By contrast, BLM criteria should more accurately yield the level of protection intended to protect and maintain aquatic life uses over a wider range of water chemistry conditions, and should, therefore, be neither under-protective nor over-protective.

Figure 1: BLM conceptual model (From Santore[19] and Pagenkopf 1983[20])



The EPA BLM Technical Support Document indicates that even if the biochemical receptor (where the mode of toxicity occurs) of an organism is not a gill, the principles of the model should apply to any other site of toxic action. Therefore, any derived BLM criteria would generally be protective of aquatic species despite differences in the toxic site of action. Further, the BLM has been developed and calibrated based on fathead minnow metal accumulation datasets. Fathead minnow data serve as a surrogate for other organisms because of the lack of metal accumulation studies for other aquatic organisms.

To date the BLM for copper has been calibrated with acute toxicity datasets for many aquatic organisms, including for example:

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[19] Santore, Robert. *Overview of the Copper BLM*. Presentation at EPA BLM Workshop, Seattle, WA May 13-14, 2015.

[20] Pagenkopf, G.K. 1983. Gill surface interaction model for trace-metal toxicity to fishes: Role of complexation, pH, and water hardness. Environ. Sci. Technol. 17:342-347.

- Freshwater: fathead minnow *(P. promelas)*, rainbow trout, *(Oncorhynchus mykiss), Daphnia magna, D. pulex, D. pulicaria, Hyallela azteca, Ceriodaphnia dubia,* freshwater mussel (*Lampsilis siliquoidea*), rotifer (*Brachionus calyciflorus*), pond snail (*Lymnaea stagnalis*), apple snail (*Pomacea paludosa*), white sturgeon (*Acipenser transmontanus*), and three-spined stickleback (*Gasterosteus aculeatus*).

- Saltwater: Blue mussel *(Mytilus edulis, and M. galloprovincialis), sand dollar (Dendraster), oyster, (Crassostrea gigas, C. virginica), and urchin (Strongylocentrotus purporatus)*

The BLM integrates other models to predict the amount of lethal copper concentrations on the biotic ligand. The BLM uses the Chemical Equilibria in Soils and Solutions (CHESS) model to evaluate the speciation of copper in water under varying conditions. To evaluate the complexation of copper to dissolved organic carbon, the model used the Windermere Humic Aqueous Model (WHAM) V.5. Information about the binding of copper to the gill comes from the Gill Surface Interaction Model and the Free Ion Activity Model.

Although EPA's 2007 copper recommendations are based on BLM version 2.2.1, there are additional BLM versions that have since been developed. EPA expects to update and release an updated BLM version in 2016[21]. This update will likely include:

- Additional acute toxicity data;
- Additional chronic toxicity data and a revised sensitivity distribution to replace the acute-to-chronic ratio methodology currently used to derive chronic criteria; and
- The ability to calculate a fixed monitoring benchmark (FMB) acute and chronic value, which is a probabilistic approach to account for time variability (for more information about FMBs, see section VIII.B.).

EPA has only recommended the use of the model for freshwater systems, but EPA is currently reviewing a BLM to predict copper toxicity to saltwater aquatic organisms[22].

IV.B Instantaneous Water Quality Criteria

The BLM calculates an acute and chronic criterion based on the model input parameters. The model derives the acute criterion based on EPA's methodology by dividing the final acute value by two. The final acute value represents the 5th percentile of genus sensitivities. The chronic criterion is then calculated using an acute-to-chronic ratio. The model refers to these criteria derived for a given water sample or set of input parameters as the instantaneous water quality criteria (IWQC). The model uses the term "instantaneous" because it is a criterion that is based on one sampling event, and therefore, reflects what the criterion would be at that point of time. In reality, BLM parameters, such as pH and DOC vary

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[21] EPA. Joe Beaman. *EPA Freshwater Copper BLM and Missing Parameter Documents: Status.* Presentation at EPA BLM Workshop, Seattle, WA May 13-14, 2015.

[22] Ibid.

temporally—diurnally, seasonally or hydrologically. Because of the variability of these parameters and their strong effect on copper bioavailability, it is especially important to account for this variability. For this reason, EPA recommends BLM monitoring that sufficiently captures site variability.

Copper data is not required to develop IWQC because the model is only predicting what the toxic concentration would be based on water chemistry at that site. The model generates the IWQC that would apply to a given sample, and the user must then determine how to apply results to determine a final criterion. Methods that could be used to derive a criterion include a statistic of the distribution of IWQC, such as a10th percentile or median, Monte-Carlo modeling, fixed benchmarks or other alternatives.

IV.C Required Data Inputs

The following data requirements reference the documentation for BLM model version 2.2.3,[23] but is similar to other versions. The BLM requires specification of 12 input parameters in order to calculate a water quality criterion. Only 10 of these parameters are measured constituents of water quality. Of the 10 measured parameters, two are physical properties (temperature and pH), seven are geochemical ions (Ca, Mg, Na, K, Cl, SO4 and alkalinity), and one is a measure of organic carbon (dissolved organic carbon (DOC) as measured in a filtered sample). Values for dissolved inorganic carbon (DIC) can be entered directly if known, or the model allows users to enter alkalinity. The model can calculate DIC using equilibrium constants related to alkalinity, pH and temperature. Two parameters, humic acid fraction and sulfide are currently configured to use default values. The list of BLM parameters and their calibration ranges at the time of the release of the 2007 EPA copper document are in **Table 4**. The most recent version of the BLM (3.1.2.37) also allows calculations with a reduced parameter list consisting of temperature, pH, DOC and hardness[24].

The sulfide module is not currently used in the calculation of IWQC for copper, so the model assigns a default value of $1x10^{-6}$ mg/L. The humic acid percentage of the DOC is typically set to a default value of 10% because these data are not commonly available. Ten percent is the expected proportion of humic acid represented in DOC in many natural systems[25]. The remaining DOC percentage is assumed to be fulvic acid. A user may enter measured values for the humic acid fraction when data are available.

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[23] HydroQual, Inc. (2007). The Biotic Ligand Model Windows Interface, Version 2.2.3: User's Guide and Reference Manual. Mahwah, NJ, HydroQual, Inc.

[24] http://www.windwardenv.com/biotic-ligand-model/

[25] Leenheer, J. A. and J.-P. Croué (2003). "Characterizing Aquatic Dissolved Organic Matter." Environmental Science & Technology **37**(1): 18A-26A.

Table 4: BLM input parameters and calibration ranges

PARAMETER	LOWER BOUND	UPPER BOUND
Temperature (°C)	10	25
pH (Standard Units)	4.9	9.2
DOC (mg/L)	0.05	29.65
Calcium (mg/L)	0.204	120.24
Magnesium (mg/L)	0.024	51.9
Sodium (mg/L)	0.16	236.9
Potassium (mg/L)	0.039	156
Sulfate (mg/L)	0.096	278.4
Chloride (mg/L)	0.32	279.72
Alkalinity (mg/L)	1.99	360
DIC (mmol/L)	0.056	44.92
Humic Acid Content (%)	10	60
Sulfide (mg/L)	0	0

Physical Properties

Temperature- the BLM is a thermodynamic-equilibrium model, and temperature determines thermodynamic reaction rates.

pH- determines chemical speciation of metals, including copper, and complexation with organic matter. As pH increases, the fraction of copper that exists as copper carbonate complexes increases, thereby reducing toxicity. Further, the deprotonation of DOC at higher pH levels increases the degree to which the copper-DOC complex forms, which reduces bioavailability as well.[26,27]

Geochemical Ions and Organic Carbon

Dissolved Organic Carbon (DOC) - forms stable organo-metallic complexes when cationic species of metals, such as copper, undergo proton binding to carboxyl and phenolic functional groups of organic molecules. Critical for determining metal speciation and bioavailability, as copper bound to DOC is not

[26]EPA (2003). The Biotic Ligand Model: Technical Support Document for Its Application to the Evaluation of Water Quality Criteria for Copper. Office of Science and Technology. Washington, D.C., United States Environmental Protection Agency**:** 72, HydroQual, I. (2009). The Biotic Ligand Model Windows Interface, Version 2.2.4: User’s Guide and Reference Manual. Mahwah, NJ, HydroQual, Inc.

[27] HydroQual, I. (2007). The Biotic Ligand Model Windows Interface, Version 2.2.3: User’s Guide and Reference Manual. Mahwah, NJ, HydroQual, Inc.

considered bioavailable. The BLM also incorporates default assumptions about the quality or character of the DOC. For example, it applies default stability constants for each organo-metallic complex.[28,29,30]

Humic acid fraction – describes the organic matter quality and chemistry. Humic acids have fewer phenolic binding sites relative to fulvic acids and reduce the binding capacity for copper when they make up a high proportion of DOC. The BLM uses a default value of 10%, although a user can input measured humic acid data if available.

Geochemical Cations (Ca, Mg, Na, K) – cations, especially the hardness cations Ca and Mg, compete with free copper cations for binding on receptor sites on the biotic ligand of organisms. Ca, Na, and Mg directly complete with Cu at biotic ligand receptor sites. Potassium is included to account for ionic balance, which can affect copper speciation.

Geochemical anions (SO_4, Cl) – are necessary for determining charge balance and ionic strength of water samples, which affects the speciation of copper to forms that are bioavailable and bind with the biotic ligand.[23 30]

Alkalinity- used by the model to calculate the dissolved inorganic carbon (DIC) in the BLM model. DIC contributes to the formation of stable copper carbonate complexes. These complexes reduce the bioavailability of copper ion.[30]

Sulfide – complexes with many metals, including copper, and the behavior of sulfide and sulfide complexes in surface waters is an emerging field of study. Sulfide is included in the model as a placeholder for future expansion, but does not factor into IWQC calculations at this time. However, a non-zero number must be input into the model, so the BLM assigns a default value of $1x10^{-6}$ mg/L.[30]

The BLM assumes using dissolved concentrations of all parameters (filtered through a 0.45 µm membrane filter). These are expected to be more representative of the water chemistry and bioavailability of copper. Total concentrations of parameters can be significantly higher than dissolved concentrations under certain conditions.

IV.D Fixed Monitoring Benchmark

Version 2.2.4 of the BLM incorporates a Fixed Monitoring Benchmark calculation in addition to an IWQC. The FMB is a probability-based calculation that accounts for time variability in BLM-predicted IWQCs relative to concurrent in-stream copper concentrations. The FMB partially depends on observed

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[28] EPA (2003). The Biotic Ligand Model: Technical Support Document for Its Application to the Evaluation of Water Quality Criteria for Copper. Office of Science and Technology. Washington, D.C., United States Environmental Protection Agency**:** 72.

[29] EPA (2007). Aquatic Life Ambient Freshwater Quality Criteria - Copper. Office of Water, United States Environmental Protection Agency. **4304T**.

[30] HydroQual, I. (2009). The Biotic Ligand Model Windows Interface, Version 2.2.4: User's Guide and Reference Manual. Mahwah, NJ, HydroQual, Inc.

copper concentrations, whereas IWQC are generated independent of copper concentrations, and depend only on the chemical characteristics of the water at a site. For this reason, copper data must be available. The FMB extrapolates an observed frequency distributions to estimate a constant copper concentration that is defined such that in-stream dissolved copper concentrations at or below the FMB will not exceed the time-variable IWQC more frequently than a selected target exceedance frequency, (e.g. 1 in 3 years, which is a common recurrence interval for the aquatic life criteria) (**Figure 2**). Version 2.2.4 of the BLM software estimates the FMB by calculating a toxic unit (TU), which is the ratio of the copper concentration in the sample to the IWQC generated by the model for that water sample. The distribution of TU values for all of the samples collected at a site is used to estimate the probability that an in-stream copper concentration will equal or exceed its associated IWQC, based on assumptions of a log-normal distribution. For samples with a TU greater than one, the in-stream copper concentration exceeds the corresponding water quality criterion for that sample. By looking at the distribution of TU values for the entire dataset, an extrapolation estimating the potential of exceedance can be compared to the target exceedance frequency. In Figure 2, dashed lines represent revised distributions that meet the specified exceedance frequency of once every three years. The benchmark is defined as the concentration at which the revised dissolved copper distribution intersects the desired exceedance frequency.

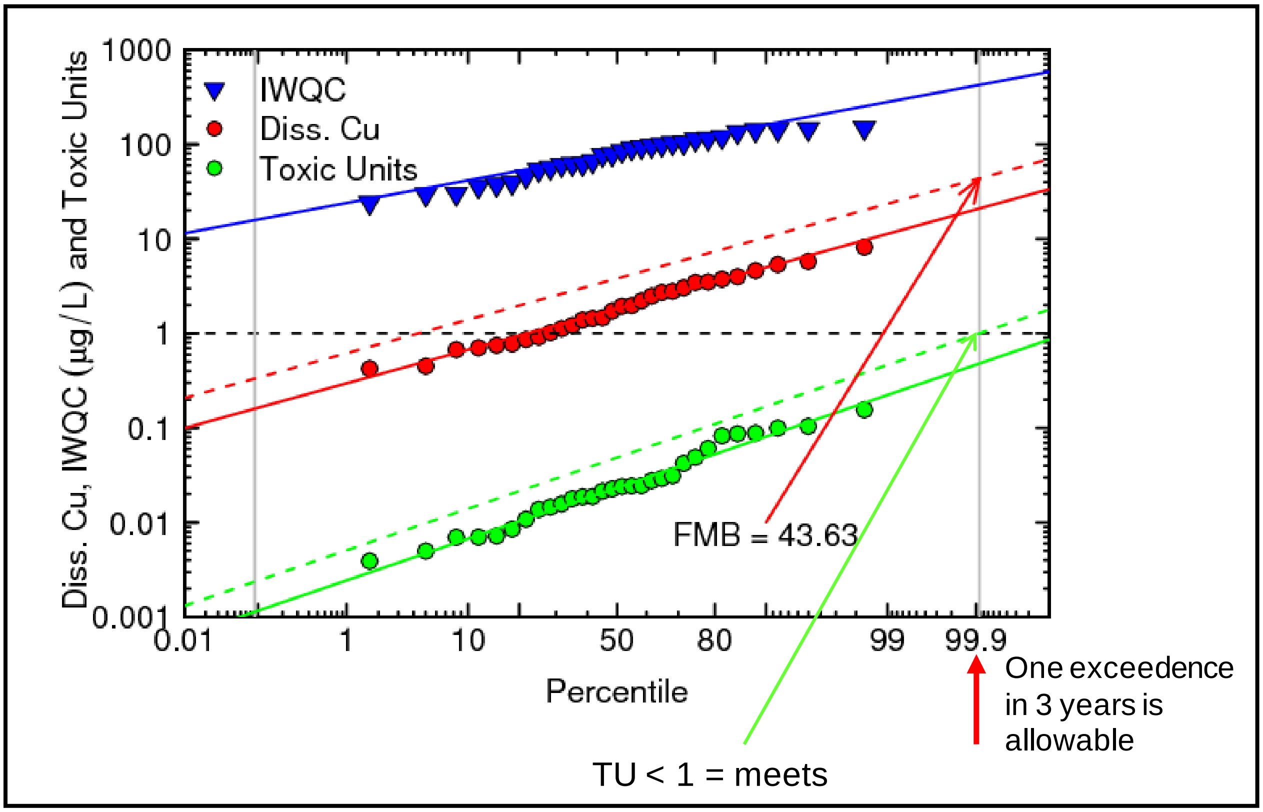
If the distribution of TU exceeds 1 at a higher frequency than the target exceedance frequency, then the value of the benchmark will be lower than the copper concentration associated with the current once in three year TU value. This indicates that in-stream copper concentrations at the site may need to be reduced in order to be protective of aquatic life.

$$TU_i = \frac{Cu_i}{IWQC_i}$$

Where: TU > 1 = exceeds the water quality criteria
TU ≤ 1 = meets the water quality criteria

Where TU_i *= Toxic units of the ith sample,* Cu_i *= copper concentration of the ith sample, and IWQC equals the BLM-derived instantaneous water quality criteria of the ith sample.*

Figure 2: Example[31] of a FMB probability distribution plot



Work done by Santore, Ryan and others[32] show that the FMB can occur at any percentile of the IWQC distribution, and still be protective of aquatic life, as long as the toxic unit is less than one. Where the FMB occurs in this distribution is dependent on the variability of copper, IWQC and their correlation at that site.

The FMB incorporates a frequency distribution that can be compared to a selected return frequency calculation, such as a single event in three years. Therefore, this method provides information that can be used to set NPDES permit limits or determine listing status for purposes of the Integrated Report. For example, in Colorado, FMBs are currently the method of choice for development of BLM copper criteria. These site-specific criteria are subsequently being used for development of NPDES water quality based effluent limits. Currently, Oregon does not use probability plots to assess compliance with toxics or other pollutants.

Although the FMB has been developed for the copper BLM, this method could also be applied to other pollutants, such as ammonia or hardness-based metals, where criteria can change based on varying water quality characteristics.

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[31] Adam Ryan and Robert Santore. HDR Consultants. *Copper BLM, IWQC, FMB…What are the tools for?* Presentation at EPA BLM Workshop, Seattle, WA May 13-14, 2015.

[32] Ibid.

For more information about the FMB, see the User's Guide and Reference Manual[33]. An excellent source illustrating the derivation and calculation of FMBs is an EPA study of several monitoring sites in Colorado[34].

V. Data Acquisition and Processing

V.A Biotic Ligand Model Data Acquisition

V.A.1 Objectives

The objectives for DEQ's evaluation of the Biotic Ligand Model for application in developing revised aquatic life criteria for copper in Oregon are:

- Creation of a BLM database from existing archived and current monitoring data for Oregon
- Evaluate the spatial and temporal coverage of the data, and identify any data gaps
- Characterize the range and statistical distribution of the data
- Identify the most sensitive model parameters
- Identify where and how DEQ can estimate missing parameters
- Develop accurate methods for estimating missing BLM parameters
- Compare the BLM water quality criteria to the currently effective hardness-based criteria

V.A.2 DEQ Biotic Ligand Model Monitoring

In the beginning of 2014, DEQ developed a BLM monitoring plan[35] in anticipation of evaluating the model to revise the state's copper criteria. The overall goal of the monitoring plan was to augment sampling at sites where some BLM parameters had already been collected, rather than developing new monitoring sites. In addition, DEQ did not have specific funds allocated for collecting BLM data. Instead, DEQ used funding from its existing toxics monitoring program. To minimize costs, DEQ used existing monitoring networks where staff already collect samples on a regular basis. Therefore, staff chose sites from either DEQ's ambient[36] or toxics monitoring program[37]. Other data used to evaluate the BLM were

[33] Hydroqual 2009. Biotic Ligand Model Windows Interface, Version 2.2.4. User's Guide and Reference Manual.

[34] EPA. Calculation of Fixed Monitoring Benchmarks for Copper at Selected Monitoring Sites in Colorado. Office of Water. 820R12009. April 2012.

[35] The Sampling and Analysis Plan for the BLM monitoring, which also included monitoring for additional metals, and the Quality Assurance Project Plan for DEQ's ambient monitoring program are available upon request. These documents describe sample filtration (0.45 µm membrane filter), holding times, preservations, etc.

[36] DEQ's Ambient River Monitoring Network consists of 164 sites sampled six times per year, 138 of which are monitored for BLM parameters three times per year. Most sites are near the mouth of larger rivers. For more information, see: http://www.deq.state.or.us/lab/wqm/ambientmonitoring.htm.

[37] For more information, see: http://www.deq.state.or.us/lab/wqm/toxics.htm.

obtained from both DEQ and USGS previously sampled sites based on other sampling projects. For more details about model data assembled outside DEQ's BLM-specific monitoring plan, see Section V.A.2.

Using the ambient and toxics monitoring network, DEQ selected monitoring locations for generating new BLM data sets or augmenting partial existing BLM datasets based on the following approaches:

1. NPDES discharge sites

DEQ's ambient monitoring locations act as integrator sites to represent major land uses, and therefore, tend to be located in downstream river reaches. Because most permitted storm water, municipal and industrial discharges are often located lower in the watershed, the ambient monitoring sites and some toxics monitoring sites where DEQ collected BLM data may represent waterbodies influenced by a mix of point and nonpoint sources. These sites also indicate water quality conditions where a large proportion of permitted discharges will occur. Therefore, this dataset provides information about sites already impacted by human activity, and BLM generated results will reflect such conditions.

For this reason, DEQ sought to collect or augment BLM data at monitoring locations close to NPDES effluent discharge sites[38]. DEQ did not inquire whether these dischargers were already collecting data for BLM purposes. Several dischargers have extensive data sets of the BLM parameters. DEQ typically chose sites upstream of the discharger because upstream data provided an indicator of the potential assimilative capacity prior to the influence of a discharge. DEQ recognizes that the discharge quality can influence the derivation of BLM criteria and downstream data may therefore provide a better indicator of conditions. However, in absence of downstream data, permitting staff can model downstream BLM parameters through a mixing analysis if upstream and effluent BLM parameters are collected[39].

If sites downstream of a discharger had more BLM data, were closer to the point of discharge, or there were no monitoring sites upstream of the discharge, then DEQ chose the downstream site. In addition, DEQ focused on municipal wastewater dischargers that have a design averaged dry seasonal flow rate of one million gallons per day (0.52 m^3 sec^{-1}) or greater because these larger systems have toxics monitoring requirements, including copper. Industrial wastewater discharger toxics monitoring requirements are more complex, and could not be categorized as easily, so DEQ generally prioritized these sites higher even if toxics monitoring requirements were not known. Many municipal and industrial dischargers are located in highly urbanized portions of the Willamette River basin, so this area had more representation in the database than other parts of the state.

2. Sites with existing copper data

DEQ collected BLM parameters at many sites with existing copper data. This served several purposes. One purpose was that DEQ could potentially develop BLM FMBs at sites with copper data.

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[38] Oregon DEQ Source Information System (SIS) database: http://www.deq.state.or.us/wq/sisdata/sisdata.asp

[39] Note that water quality conditions can change significantly downstream of a discharge, so in an ideal situation, BLM monitoring points would include both upstream and downstream of a point source and the effluent.

In addition, for purposes of the Integrated Report, if adequate data are available, DEQ could develop criteria in order to assess waterbody conditions at sites with existing copper data.

3. Augment sites with existing BLM data or at sites with no BLM parameters

DEQ primarily sampled at locations where some important BLM parameters, such as DOC or pH, were already collected in order to develop larger datasets for modeling. However, DEQ also collected data at some sites where there were no BLM data for an entire water body.

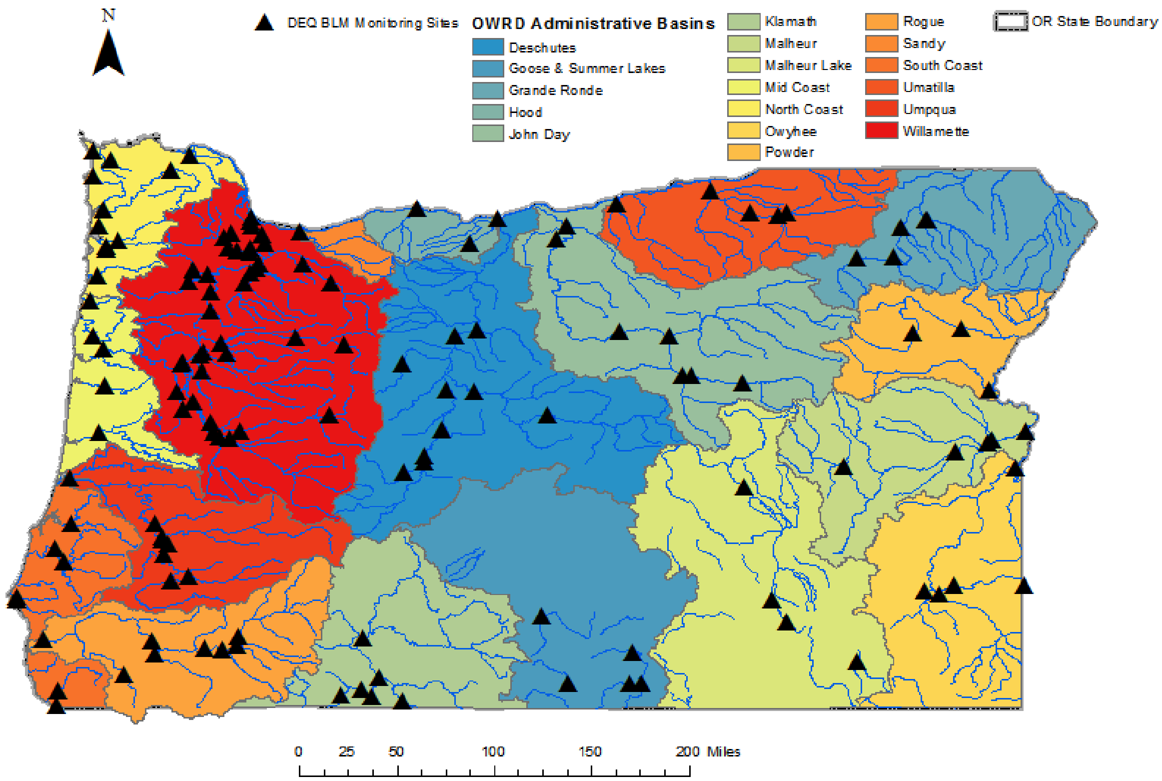
4. Sites in upper stream reaches

DEQ sought to collect or augment BLM data in streams farther up in the watershed and streams where there were no permitted discharges to gain insight on areas with fewer anthropogenic impacts. Although some of these sites are represented, particularly water bodies where there are no point sources, due to resource constraints and priority for point source inputs, these sites are not as well represented.

As a result of the preceding location selection approaches, DEQ is sampling at 138 sites across the state, three times a year for two years for a total of six sampling events from July 2014 – June 2016 (**Figure 3**).

BLM anion parameters (sulfate and chloride) were collected at about half of the sites due to analytical constraints at the lab. Lab staff collected both total and dissolved BLM parameters to determine how the dissolved versus total concentrations related to each other and whether these expressions could be interchanged depending on the relationship. For example, could a relationship between total organic carbon (TOC) and DOC be established? If so, historical TOC data, which is much more common than DOC analyses, could be used to estimate DOC when not available (see DEQ analysis in section V.B.5.).

Figure 3: Map of DEQ BLM monitoring locations



V.A.3 Sites in the Oregon Database

The initial data screening requirements identified data from 812 sampling locations with multiple samples collected at many of the sites (**Table 5**). These sites are distributed across the state, with representation in each of the administrative districts used by the Oregon Water Resources Department (**Figure 4**). The boundaries shown are administrative in nature and provided for context only. They are not designed for use in hydrologic analysis or similar analyses even though they may correspond with drainage delineations.

Figure 4: Map of Biotic Ligand Model sites from various data sources

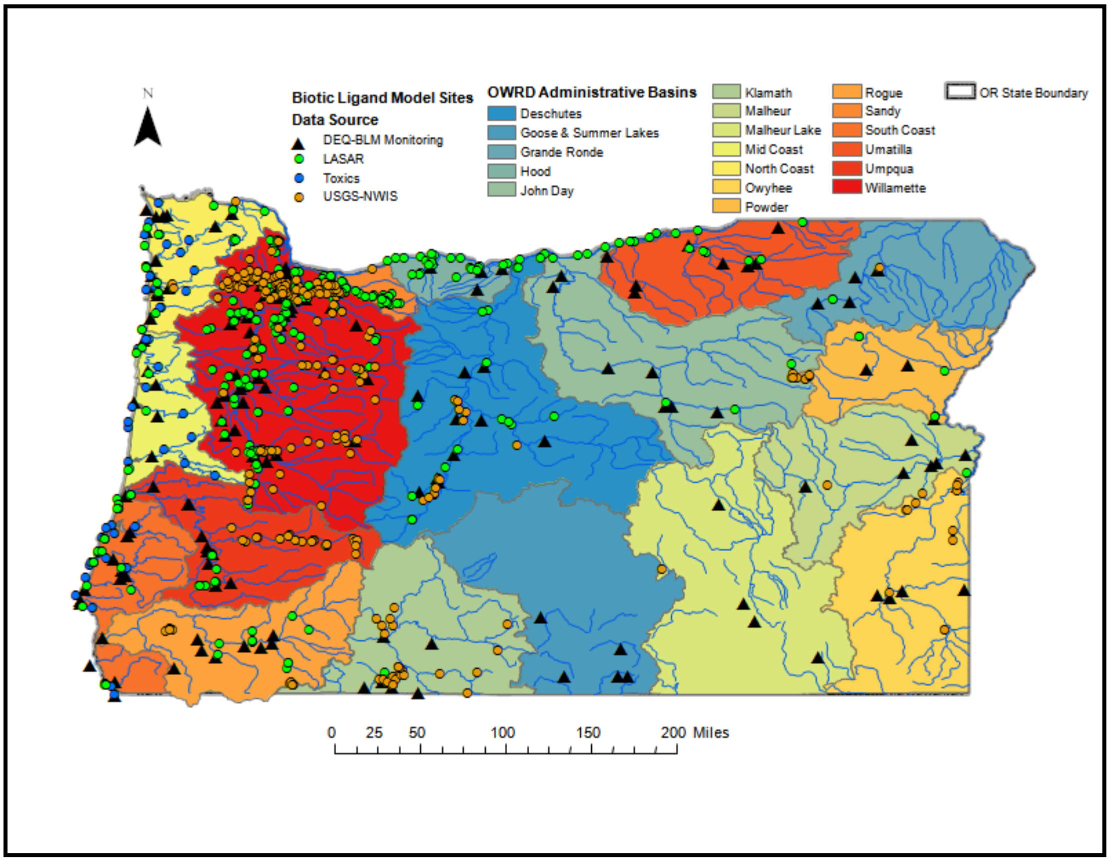


Table 5: Sites in the Oregon BLM database

OWRD Basin	Sites (n)
Deschutes	47
Goose and Summer Lakes	5
Grande Ronde	8
Hood	27
John Day	17
Klamath	39
Malheur	9
Malheur Lake	5
Mid Coast	24
North Coast	48
Owyhee	16
Powder	15
Rogue	30
Sandy	37
South Coast	42
Umatilla	21
Umpqua	55
Willamette	367
Total Sites	**812**

V.B. Database Quality Assurance and Quality Control

V.B.1 Data Sources and Quality Assurance

In order to acquire enough data to evaluate the BLM model and calculate water quality criteria, existing data from within the State of Oregon were collected from two sources: the Oregon DEQ LASAR database and the USGS-NWIS database (see **Table 6** and **Table 7**). The Oregon DEQ also initiated collection of BLM parameters at 138 sites across the state as part of its ambient monitoring program in October of 2014, but data for BLM parameters are available at some sites starting in October 2013.

Historical data from the DEQ and USGS databases were initially screened for the following characteristics:

- Sites within the state of Oregon
- Samples collected between 2000-2015. This time frame generally represented more current conditions and included data with lower reporting limits. This was particularly important for DOC data.[40]
- Sites identified as fresh, surface waters including lakes, rivers and streams

[40] USGS (1999). New Reporting Procedures Based on Long-Term Method Detection Levels and Some Considerations for Interpretations of Water-Quality Data Provided by the U.S. Geological Survey National Water Quality Laboratory. Open File Report 99-193, U.S. Geological Survey.

- Samples with a high QA/QC rating by their agency of origin. For DEQ, data A+, A or B quality control grades. [41] For USGS, data result status was "accepted", indicating it passed with respect to USGS QA/QC criteria.[42]
- Samples with concurrent measurements of at least one BLM input parameter, specific conductance and temperature
- Specific conductance less than 1500μmhos/cm, so that sites potentially influenced by marine waters would be excluded as well as samples that might represent sources, such as landfill leachate, untreated wastewater, and other potentially highly contaminated samples, rather than receiving waters.

Following this initial screening, there were 823 sites from all sources that were sampled in Oregon since January of 2000 that include at least TOC or DOC, pH and temperature data. A table showing the number of samples for each parameter per monitoring site is available in Appendix A.

Table 6: Data sources for the Oregon Biotic Ligand Model database

Number of sites from each data source with at least organic carbon, pH and temperature data	
DEQ BLM Monitoring Sites	138
DEQ Other Ambient	26
DEQ Toxics	41
DEQ LASAR	413
USGS-NWIS	306
Total Unique Sites	**812**

[41] Hoatson, S. (2013). Data Validation and Qualification. Oregon Department of Environmental Quality Guidance, Oregon Department of Environmental Quality.

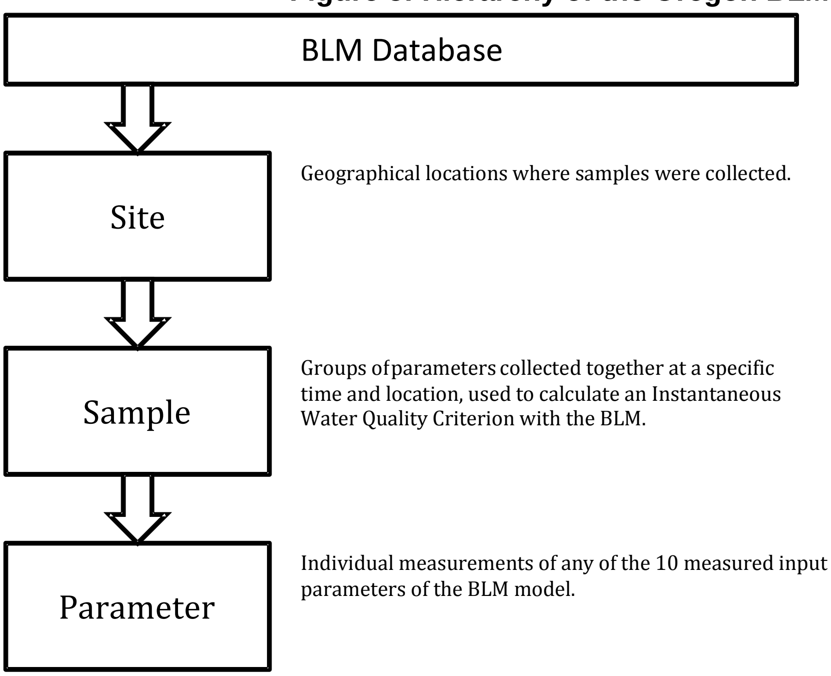
[42] USGS (variously dated). National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations. Book 9. available online at http://pubs.water.usgs.gov/twri9A, U.S., Geological Survey.

Table 7: Dates and sample sizes for the Oregon Biotic Ligand Model database

Date ranges and number of samples with concurrent DOC or TOC, pH and temperature data				
Agency	**Data Source**	**Start Date**	**End Date**	**Samples (n)**
DEQ	BLM and ambient monitoring	Oct. 2013-	Present	14,674
DEQ	Toxics BLM	Jan. 2013-	Oct. 2014	2,255
DEQ	LASAR	Jan. 2003-	Sept. 2013	13,215
USGS	NWIS	Jan. 2000-	Sept. 2014	125,311
All	**Total Samples**	**Jan. 2000-**	**Present**	**155,455**

The resulting Oregon BLM database is spatially organized by unique site identifiers assigned by the collecting agencies and lat/long location, and temporally by the date of sampling (**Figure 5**). Multiple samples may have been collected at a particular site over time. Samples are defined as concurrent measurements of one or more of the individual BLM parameters made on a certain date at a particular site. Each sample may be able to serve as the basis for calculating a water quality criterion with the BLM depending on completeness of the required BLM parameters and findings of the subsequent sensitivity evaluations of each parameter, and estimation approaches for missing parameters.

Figure 5: Hierarchy of the Oregon BLM database



V.B.2 Data Use Methodology

DEQ combined raw data acquired from the USGS and DEQ databases into a common database that allowed for interchangeability between agency sources and matching the format required for input to the

BLM. The following section describes the procedures used to prepare data from different agency sources for analysis. Analyses and data manipulation were conducted in the R statistical environment.[43]

The conditioning of raw data into a format suitable for BLM input included:

1) Conversion to common units
2) Handling of non-detect data
3) Interchangeability of total and dissolved measures of geochemical ion parameters

The results of the above manipulations yielded the “conditioned” Oregon BLM database, which DEQ then evaluated for:

1) Range and statistical distribution of the BLM parameters
2) Temporal representation of the data
3) Completeness of the data
4) Sensitivity of the BLM to the range and distribution of data.

This database was sub-divided for different analyses depending on the availability of measured parameters and the particular data needs of each analysis.

These sub-divisions were:

1) The initial database, consisting of the measurements of any BLM parameter available after the initial screening of the raw data, without regard to whether the parameter was of total or dissolved form, or the number of other parameters in a particular sample. The median number of BLM parameter measurements at each site was 19, although some sites were included if they had specific conductance data and at least one other measured BLM parameter. This database was used to determine the correlation of total and dissolved parameters (section V.B.5.).

2) The conditioned database (**Table 14**), is the main database for the BLM and consists of samples from the initial database after quality assurance adjustments were applied to censored values (section V.B.3.), total and dissolved data (section V.B.5.) and outliers and extreme values (**Figure 19**). This database includes all samples with measured results for at least one BLM parameter. The database was used for assessing data completeness (section V.C.2), conductivity correlations (section VI.A), regional patterns in the distribution of parameters (section VI.B), temporal variability (section VIII.B.2). Missing parameters were estimated for samples in this database to provide additional data for calculating IWQC (section VI.).

3) Completely measured BLM samples, consisting of only those samples where all 11 BLM parameters were measured (**Table 16**). This limited database was used for analyses requiring comparison of BLM outputs based on estimated parameters with actual values. These include parameter sensitivity (section V.C.1), comparing paired hardness-based criteria with BLM IWQC (section VIII.B.), and evaluating the effect of using regional estimates of parameters as default inputs (section VI.B).

[43] R Development Core Team (2015). R: A language and environment for statistical computing. Vienna, Austria, R Foundation for Statistical Computing.

V.B.3 Analytical Limits and Use of Censored Results

The Reporting Limit/Quantitation Limit (QL) of an individual analytical procedure is the lowest amount of analyte in a sample that can be quantitatively determined with suitable precision and accuracy. The detection limit (DL) is the lowest quantity of a substance that can be distinguished from a blank sample of known zero concentration. It reflects the concentration at which the signal of a substance can be determined from background noise.

When a sample value occurs between the QL and DL, it is determined to be present in the sample, but its concentration cannot be determined with acceptable certainty. DEQ flagged all samples with a concentration that falls below the QL as censored. That is, the concentration values in the database are not reliable. Parameter values that are recorded at or below the quantitation limit (QL) have the potential to bias calculation of both the IWQC for that sample,[44] and more crucially, the calculation of fixed monitoring benchmarks.[45] For most parameters, only a small number of parameters had concentrations between their respective QL and DL (**Table 8**).

Table 8: Censored data results

Censored Results by Parameter					
Parameter	**Samples**	**# Censored**	**% Censored**	**Below QL**	**Below DL**
Alkalinity	18,869	2	0.01 %	2	0
Chloride	17,401	165	0.95 %	160	5
Specific conductance	21,504	182	0.008 %	182	0
Hardness	2,621	10	0.38 %	10	0
Potassium	1,158	35	3.02 %	16	19
Sodium	1,431	6	0.42 %	6	0
Sulfate	1,745	6	0.34 %	1	5
DOC/TOC	6,731	1,616	24.0 %	1,408	208
DOC	2,375	172	7.2 %	130	42
TOC	4,356	1,444	33.1 %	1,278	166
Copper	5,968	4,252	71.2 %	4,245	7

Geochemical Ions

The geochemical ions typically have less than 1% of parameters identified as censored (**Table 8**). Given the low rate and the insensitivity of the BLM to these parameters, this level of censoring is not expected to adversely affect calculation of IWQC.

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[44] HydroQual, I. (2007). The Biotic Ligand Model Windows Interface, Version 2.2.3: User's Guide and Reference Manual. Mahwah, NJ, HydroQual, Inc.

[45] EPA (2012). Calculation of Fixed Monitoring Benchmarks for Copper at Selected Monitoring Sites in Colorado. Office of Water, United States Environmental Protection Agency. **4304T**.

Organic Carbon

TOC and DOC had a combined rate of censored samples of 24%. The DEQ reports values of DOC down to a QL of 2.0 mg/L, which is higher than the 0.33 mg/L QL reported for a majority of samples from the NWIS database; provided by the USGS and Clean Water Services.

The DL for DOC at the DEQ analytical lab is ~1 mg/L. However, the DL used by DEQ's third party lab is lower, at 0.11 mg/L. Raw estimated concentration values between 1.0 mg/L and 0.11 mg/L exist for many samples officially reported by the DEQ at the QL of 2.0 mg/L. The USGS reported DOC concentrations down to analytical detection limits (DL) of 0.05 mg/L to 2.0 mg/L depending on the method and laboratory used, with the 0.05mg/L DL being the most common. The calibrated range of the BLM for DOC is 0.05 mg/L, about half the analytical DL of most DOC samples in the DEQ database.

IWQC calculated using DOC values at the detection limit will be biased toward lower values. Due to the inability to measure accurate DOC concentrations below the QL of ~2 mg/L, the range of minimum IWQC values is limited to the lowest IWQC that can be calculated at this concentration. This may create a bias in the lower range of IWQC values due to the sensitivity of the BLM to DOC concentration. IWQC calculated for samples where the DOC concentration in the environment is actually lower than the QL value may not be adequately protective of aquatic life. However, the number of TOC/DOC samples at the QL does not pose a major concern for estimating summary statistics of DOC because they are only a small percentage of total samples.

Copper

Copper had a high number of censored values, with a rate of 71% of parameter samples. This is not necessarily unexpected for this parameter, as many ambient water samples have copper concentrations measured at or below the DL. However, an inability to quantify copper at very low concentrations can be problematic for assessing compliance with IWQC that are near the QL for copper, and for FMB determinations. A large number of censored parameters can bias the summary statistics required for the FMB calculation. A study by the Colorado Department of Public Health and Environment and EPA found that FMBs could be accurately estimated using Maximum-likelihood Estimation (MLE) regression techniques as long as no more than 80% of copper samples were censored.[46]

Proposed Methods for Handling Censored Data

For the geochemical ions in the Oregon database, DEQ assigned a flag to censored samples below the QL for the method used in each analysis, in order to identify these samples in the database. These samples were assigned the value of the QL when less than 10% of values for the parameter were identified as being below the QL (**Table 8)**. For parameters where there were paired total and dissolved results, and one of those values was above the DL, DEQ used that value.

For organic carbon, where raw concentration data between the QL and DL was available, DEQ substituted the value of DOC with the raw data, but flagged the sample as censored. Samples reported

[46] EPA (2012). Calculation of Fixed Monitoring Benchmarks for Copper at Selected Monitoring Sites in Colorado. Office of Water, United States Environmental Protection Agency. **4304T.**

below the QL were assigned the QL value of 2.0 mg/L and also flagged as censored. Samples reported as below the DL were assigned the value of the detection limit, typically 1.0 – 0.11 mg/L, and flagged as censored.

DEQ compared the summary statistics of organic carbon data for this substitution to the estimate of the sample mean using MLE and other typical procedures for assigning values to censored data below the QL (**Table 9**). The other methods were assigning the DL to each censored sample, or ½ of the DL to each censored sample. The method described above had the lowest percent bias for the mean of the organic carbon data compared to the MLE estimate (see **Table 9**). Consequently, DEQ does not expect our substitution method, described in the preceding paragraph, for organic carbon non-detect samples to significantly bias the mean and distribution of the data.

Table 9: Comparison of estimated parameter means for organic carbon samples from various non-detect substitution methods

Substitution Method	Parameter Mean (mg\L)	Percent Bias
*Maximum Likelihood Estimate (MLE) of mean	3.93	—
Raw data reported at QL (1-2mg\L), no substitutions	3.63	7.6%
Proposed method, raw data between QL and DL	3.66	6.8%
substitute DL (0.11mg\L)	3.52	10.4%
substitute ½ DL (0.055 mg\L)	3.51	10.7%
* For estimating summary statistics only, cannot be used to assign values to specific samples		

For copper, DEQ followed the same procedure as for DOC/TOC above. First, where a sample had paired total and dissolved results of copper, and total copper was above the QL and dissolved copper was below the QL, DEQ applied a translator to estimate the value of dissolved copper from the total copper (see section V.B.5 and section VIII.C.1). Second, when raw estimated concentration data between the DL and QL was available, DEQ substituted the estimated value. Finally, where both total and dissolved measurements of copper for a parameter were below the QL or DL, the value of the QL or DL was assigned, respectively. All samples adjusted in this way were flagged as censored in the database, so that samples where copper was not detected at a quantifiable limit could be accounted for when calculating the FMB. The parameter mean and percent bias for substitution of censored copper data is compared with the MLE of the sample mean, below (**Table 10**). For comparison, DEQ also calculated the effect on parameter means of substituting all censored data with either the DL or one-half DL. These substitution methods resulted in mean copper concentrations significantly lower than both our substitution method and the raw parameter mean. Consequently, DEQ expects the substitution method to provide a reasonable estimate of the mean and distribution of the available copper data.

Table 10: Comparison of estimated parameter means for copper samples from various substitution methods for censored data

Substitution Method	Parameter Mean (µg\L)	Percent Bias
*Maximum-likelihood Estimate (MLE) of mean	2.00	—
Raw data reported at QL, no substitutions	2.06	3%
Proposed method, raw data between QL and DL	1.68	16%
substitute DL	1.23	38.5%
substitute ½ DL	1.21	39.5%
* For estimating summary statistics only, cannot be used to assign values to specific samples		

V.B.4 Range and Distribution of the Data

Figure 6 shows histograms of the log-transformed data for the geochemical ions, copper, DOC and specific conductance at 25ºC, herein referred to simply as specific conductance, from the full conditioned database. Quantile-quantile plots (**Figure 7**) show the quantile distribution of data for each parameter compared to a theoretical type of distribution. When the plot of quantiles of the distribution matches the theoretical distribution, and reasonably approximates a straight line, then the type of distribution of the data is the same as the theoretical distribution. The 1:1 line is shown as a red line and 95% confidence intervals are shown as black lines. The appearance of a break in the quantile distribution, depicted as two different slopes, for DOC, pH, alkalinity, Na^+, Cl^- and SO_4^{-2} indicates a long tail and slight departure from lognormality for high concentrations of those parameters. Temperature fits a normal distribution, and specific conductance and SO_4^{-2} resembled a Weibull distribution, which for statistical purposes is similar to a normal distribution in many cases.

Figure 6: Histograms of log-transformed parameter distributions of the conditioned database

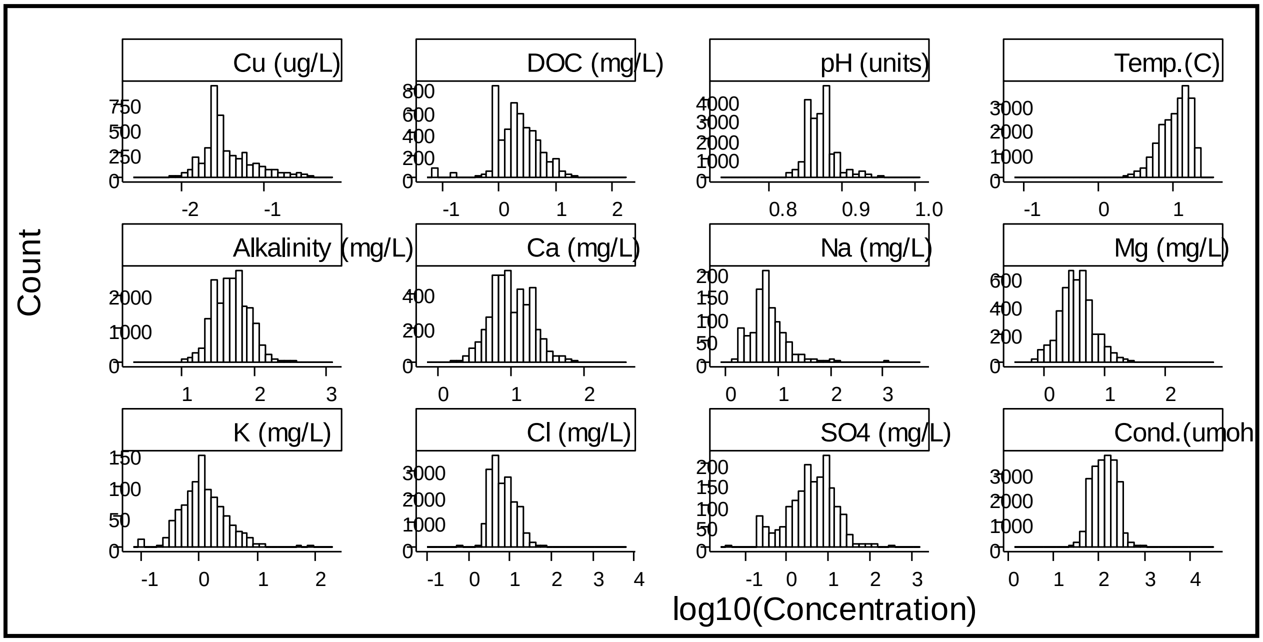
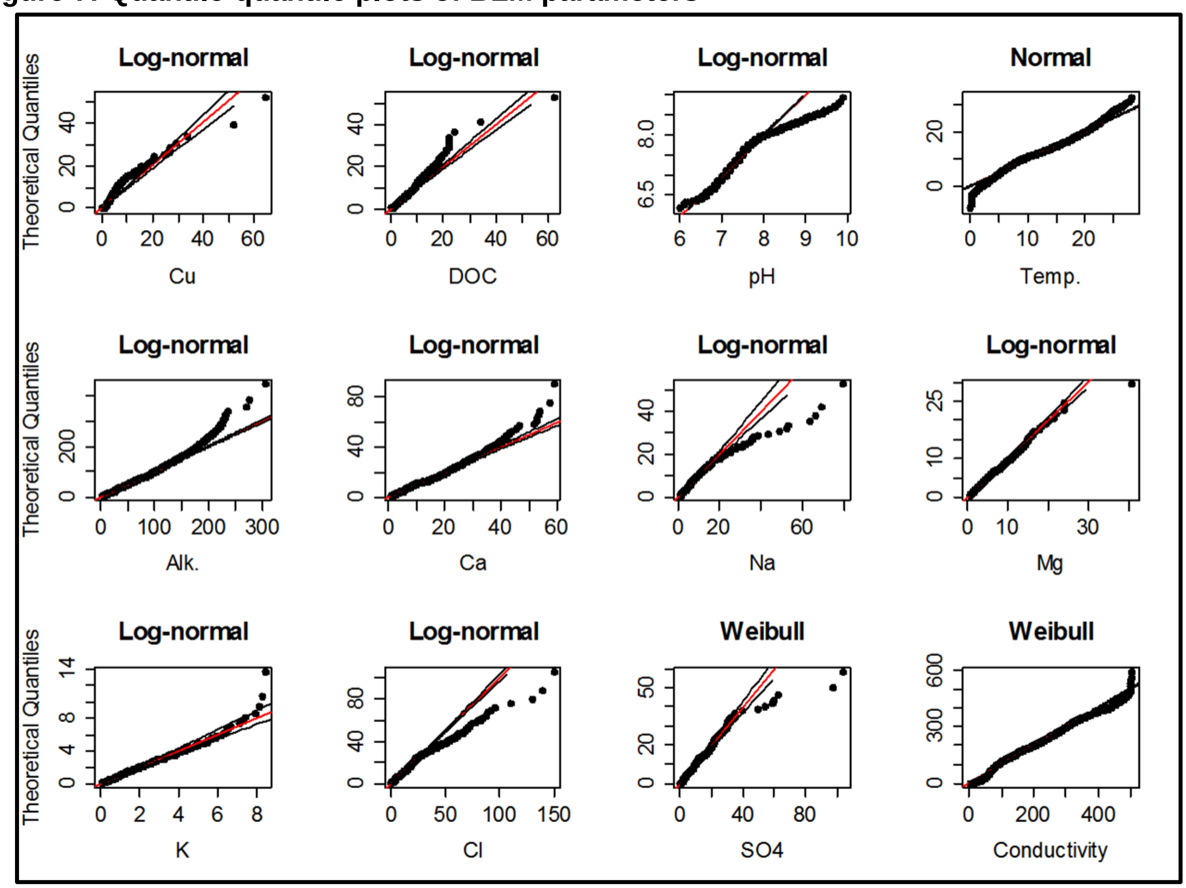


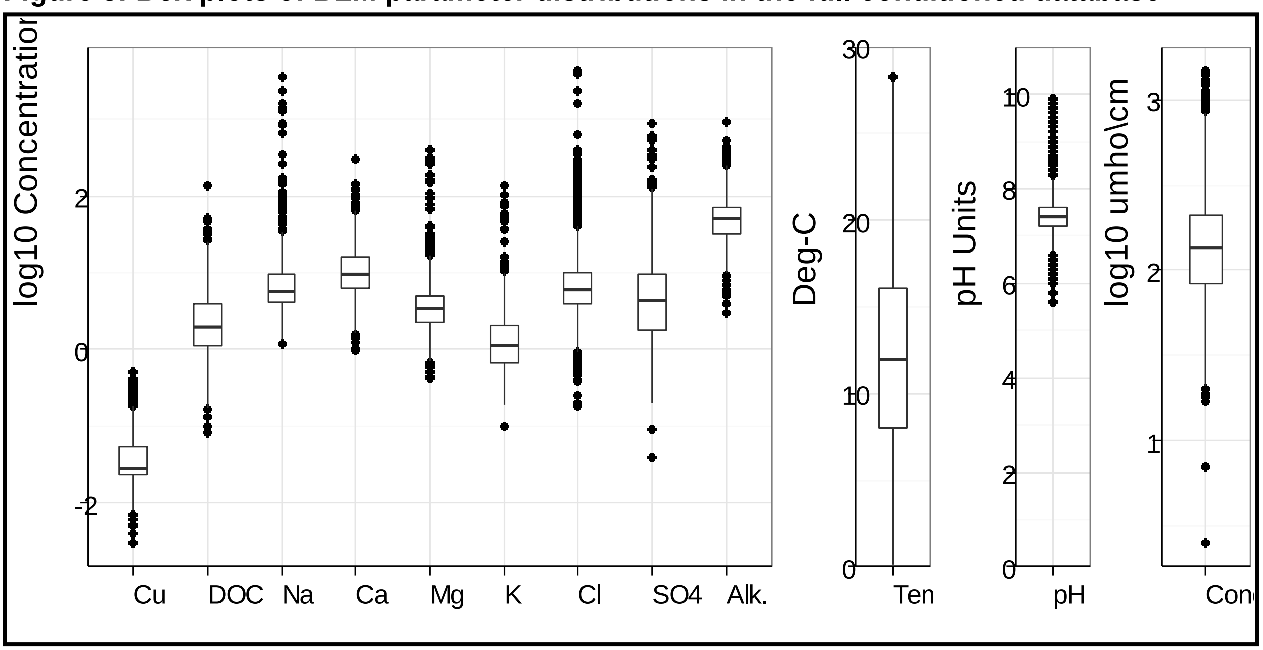
Figure 7: Quantile-quantile plots of BLM parameters



Slight bimodality was apparent in some water quality parameters, notably pH, Ca^{+2} and SO_4^{-2}, and could be a product of correlation to high and low stream discharge conditions. High volumes of discharge dilute the concentration of some parameters and increase the concentration of others relative to low volumes of discharge.[47] DEQ hypothesizes that high/low discharge regimes could be the cause of the bimodal character of the distributions seen for some of the BLM parameters in the DEQ database. DEQ was not able to calculate separate medians for each mode of these distributions, since DEQ does not have adequate stream discharge data to differentiate these regimes. Using the date to determine whether a parameter was collected in the "wet" or "dry" season as a proxy for stream discharge did not predict which mode in the distribution a given parameter measurement would be found.

The median value provides a measure of central tendency that will not be biased by extreme outliers in the data. Outliers are often observed in environmental data sets such as our parameter data, which are log-distributed with the exception of temperature. **Figure 8** shows box plots of the range and distribution of concentration for each BLM parameter in the database. The black dots represent outlying data points greater than 1.5 times the inter-quartile range of the data set (i.e. outside the range where 95% of the data values are distributed). The two "whiskers" are the limits of 1.5 times the inter-quartile range; the lower "box" represents the 25th percentile; the middle bar represents the sample median, or 50th percentile; the upper "box" represents the 75th percentile. It is important to note that DOC, temperature, and pH contain values outside of the calibrated range for BLM inputs (see **Table 4**). For evaluation purposes, these values have been included in the database. Using sample parameter values that are outside the calibration range of the BLM will need to be considered on a case-by-case basis.

Figure 8: Box plots of BLM parameter distributions in the full conditioned database



[47] Hem, J. D. (1985). Study and interpretation of the chemical characteristics of natural water, Department of the Interior, US Geological Survey.

V.B.5 Total versus Dissolved BLM Data Evaluation

The parameters measured for organic carbon, copper, and the geochemical ions in many samples in the database are measures of unfiltered/total recoverable concentration rather than filtered/dissolved concentration of the parameters in the water column. Dissolved parameters are operationally defined by Oregon DEQ as samples filtered to a 0.45μm pore size. However, in systems with high amounts of colloidal clay this dissolved measure will include significant amounts of copper bound to these colloidal particles that will pass through a 0.45 um filter. The BLM assumes input of dissolved concentrations. Omitting all parameters reported as total would result in a much smaller sample size available for calculating IWQC. Therefore, DEQ evaluated the relationship between total and dissolved results of the BLM parameters for samples that contained both measurements. DEQ used linear regression to compare the concentration between these two results for the major BLM input parameters.

Our goal was to:

1) Determine potentially significant differences between total and dissolved concentrations, and
2) Determine whether total and dissolved concentrations of parameters can be used interchangeably in the DEQ database.

Figure 6 shows scatter plots of total versus dissolved data for each BLM parameter, plus hardness. The solid line is a 1:1 line showing where concentrations between total and dissolved concentrations would be equivalent, and the dashed line is a line of fit from an ordinary least squares (OLS) regression. Sulfate and chloride do not form precipitates; therefore, they are only measured as dissolved. **Table 11** shows the results of linear regression for each parameter. The regression relationship for each parameter is significant to a value of $p < 0.001$.

Figure 6: Relationship between total and dissolved results of BLM parameters

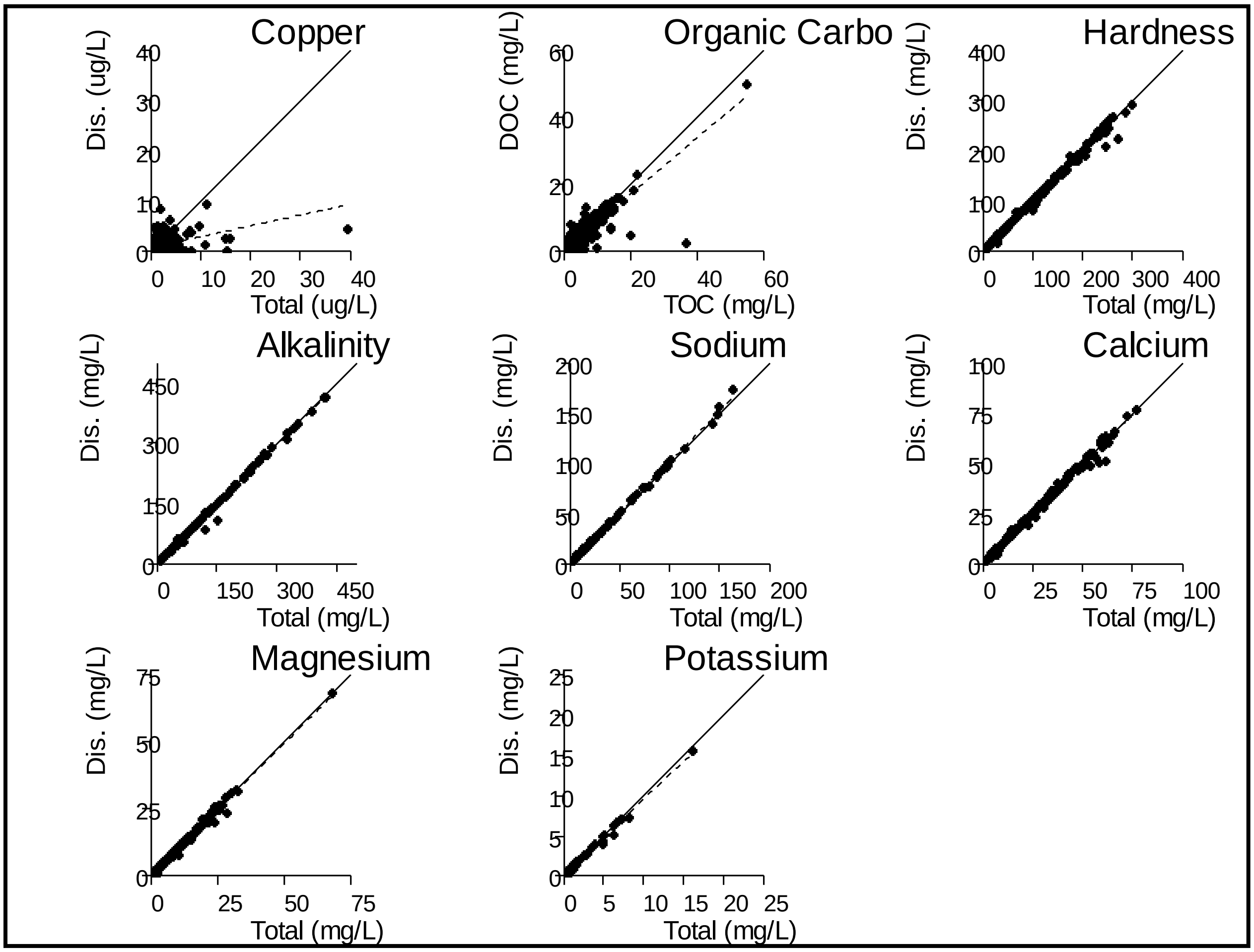


Table 11: Regression relationships between total (x) and dissolved (y) results of BLM parameters

Total (x) Versus Dissolved (y) Parameters			
Parameter	**Regression Equation**	**Adjusted R^2**	**p-value**
Copper	y = 0.771 + .2154*x	0.205	$< 1x10^{-6}$
Organic Carbon	y = 0.11 + 1 *x	0.905	$< 1x10^{-6}$
Alkalinity	y = 0.268 + 0.989*x	0.997	$< 1x10^{-6}$
Hardness	y = -0.011 + 0.989*x	0.997	$< 1x10^{-6}$
Sodium	y = -0.118+ 1.012*x	0.999	$< 1x10^{-6}$
Calcium	y = 0.035 + 0.988*x	0.997	$< 1x10^{-6}$
Magnesium	y = -0.024 + 0.988*x	0.996	$< 1x10^{-6}$
Potassium	y =-0.008 + 0.949*x	0.993	$< 1x10^{-6}$

Geochemical Ions

The total versus dissolved concentration for the geochemical ions—hardness, alkalinity, sodium, calcium, magnesium, and potassium—were very similar for all samples. There were strong regression relationships with slopes between 0.94 and 1.02 for these parameters. Adjusted R^2 for all parameters were above 0.99, although sodium appeared to show some deviation at high concentrations. Therefore, the total and dissolved results of these parameters may be used interchangeably. For BLM calculations, DEQ used the dissolved result for geochemical ions when available, and substituted the total result when samples were missing dissolved parameters.

Copper

The BLM does not require copper as input data to derive BLM criteria. However, understanding potential differences between total and dissolved copper may be helpful for evaluating the FMB for sites with long time records of samples. Differences between total (Cu_T) and dissolved (Cu_d) copper are expected because the binding affinity of copper to solids is variable and can change with site conditions. Additionally, analysis of copper utilizes trace-metal protocols that are vulnerable to contamination and are often found at concentrations near or below analytical detection limits. Filter contamination is a known issue with trace metals sample collection at the USGS and DEQ, and field methods to wash filters have been found to be helpful in reducing this contamination. These dual issues result in multiple sources of variation that can contribute to dissolved copper concentrations exceeding total copper concentrations.

To account for possible contamination or analytical noise/error at lower dissolved copper concentrations, DEQ applied a conversion factor of 0.96[48] to estimate dissolved copper from total copper data results for samples where only Cu_T were available or where $Cu_d > Cu_{T,}$. The EPA developed this conversion factor using moderately hard laboratory water. In natural systems, the dissolved copper to total copper ratio may be smaller because of copper binding to solids and organic compounds. Therefore, this conversion factor is a conservative estimate, as dissolved copper concentrations are expected to be lower than total recoverable copper concentrations. The ratio is applied in order to expand the usable data set for preliminary evaluation of the BLM. Generally, it does not reflect an evaluation of ambient partitioning of copper in the environment.

Organic Carbon

Since DOC is a highly sensitive parameter affecting the outcome of IWQC generated by the BLM, DEQ will discuss the relationship between dissolved and total organic carbon in more detail below. Overall, the correlation between total and dissolved organic carbon was somewhat strong, with an adjusted R^2 of 0.85 and a slope of 0.83 and an intercept of 0.4.

When the extreme outlier at TOC = 64mg/L is omitted, the fit improves to a slope of 1.0 with an adjusted R^2 of 0.90 and an intercept of 0.11 (**Figure 9**). In general, the correlation between total and dissolved carbon are not as strong as for the geochemical ions (**Table 11**).

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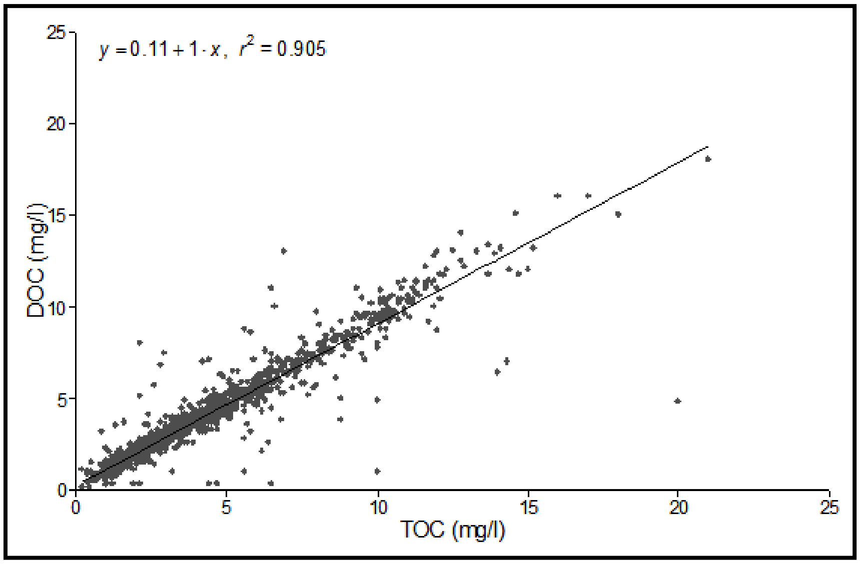
[48] EPA. 1995. Derivation of Conversion Factors for the Calculation of Dissolved Freshwater Aquatic Life Criteria for Metals. Environmental Research Laboratory—Duluth. Office of Research and Development.

Figure 9: Relationships between TOC and DOC in all samples

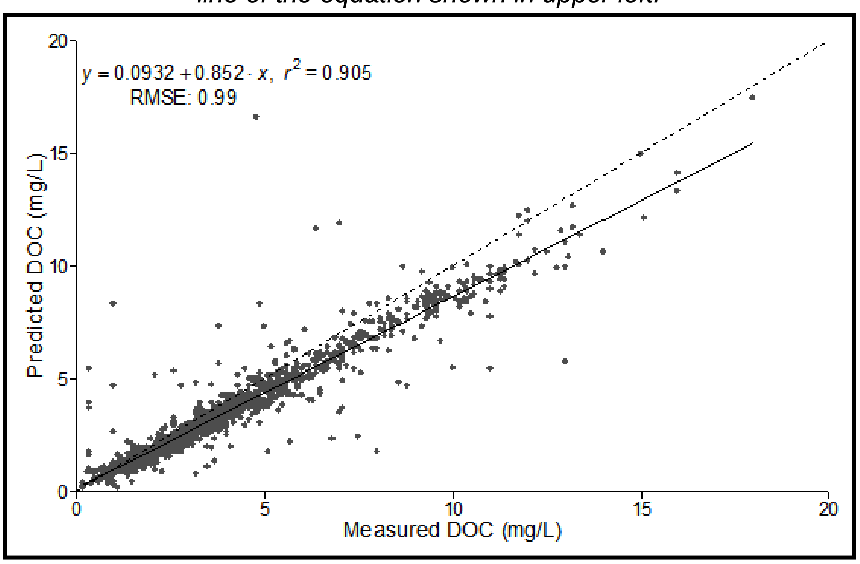
The solid line is the line of least-squares regression.



Using a translator of 0.83 was relatively accurate for predicting measured DOC values from paired TOC data (**Figure 10**). The root mean square error was 0.99 mg/L DOC, about equal to the DL of DOC for most samples.

Figure 10: Measured vs. Predicted DOC calculated using a translator of 0.83

The dashed line is the 1:1 line where predicted DOC = observed DOC. The solid line is the regression line of the equation shown in upper left.



When samples are stratified by region, it is apparent that the distribution of TOC and DOC data from the Eastern and Willamette Valley regions drive the relationship between TOC and DOC observed at the state level (**Figure 11**). There were poor adjusted R^2 values for the Coastal region, because of high dispersion which may be linked to seasonal precipitation (**Figure 14**), and for the Cascades, because of small sample size. Regression coefficients for the Eastern and Willamette Valley regions were high, 0.83 and 0.92 respectively (**Table 12**).

Figure 11: Relationships between TOC and DOC in each region

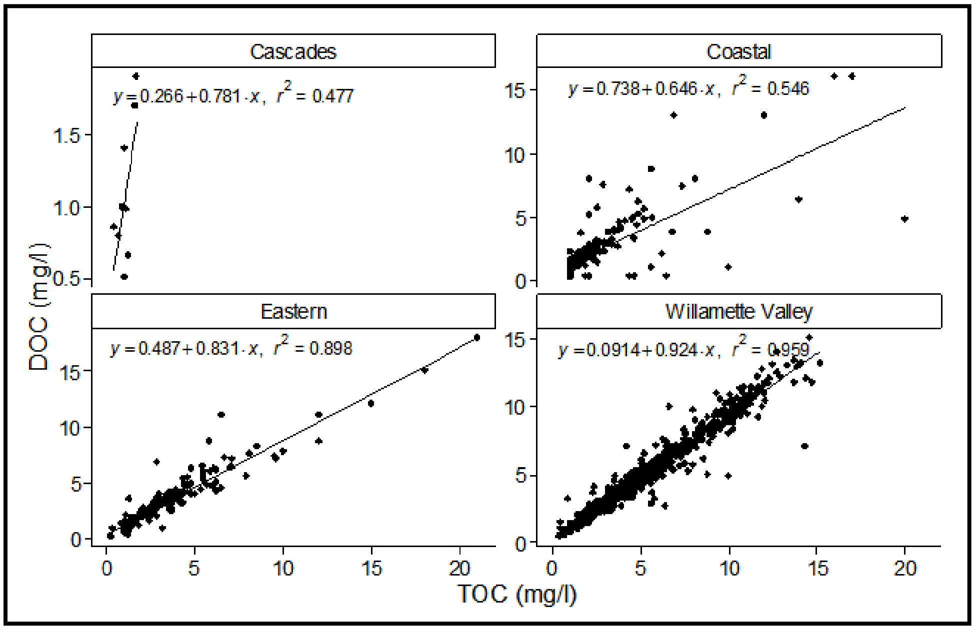
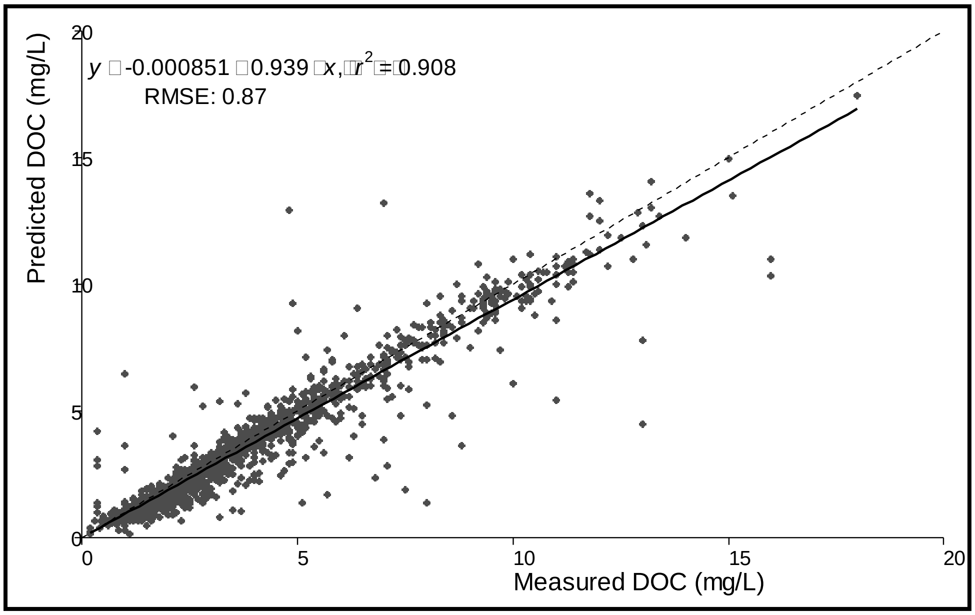


Table 12: Statistics and conversion factors based on regression coefficients of DOC and TOC for regions

Region	Median DOC	Coeff. of Variation	TOC Regression Coefficient	Number of Samples
Cascades	1.08	0.98	0.78	9
Coastal	2.35	1.6	0.64	206
Eastern	3.29	2.7	0.83	191
Willamette Valley	4.38	3.8	0.92	1,045
Statewide	**3.92**	**0.70**	**0.90**	**1,451**

Predicting DOC from paired TOC data using the individual regional translators produced a slightly more accurate estimate of measured DOC than using the statewide translator of 0.83 (**Figure 12**). While the adjusted R^2 was relatively the same, the root mean square error was about 10% lower, from 0.99 to 0.83 mg/L of DOC.

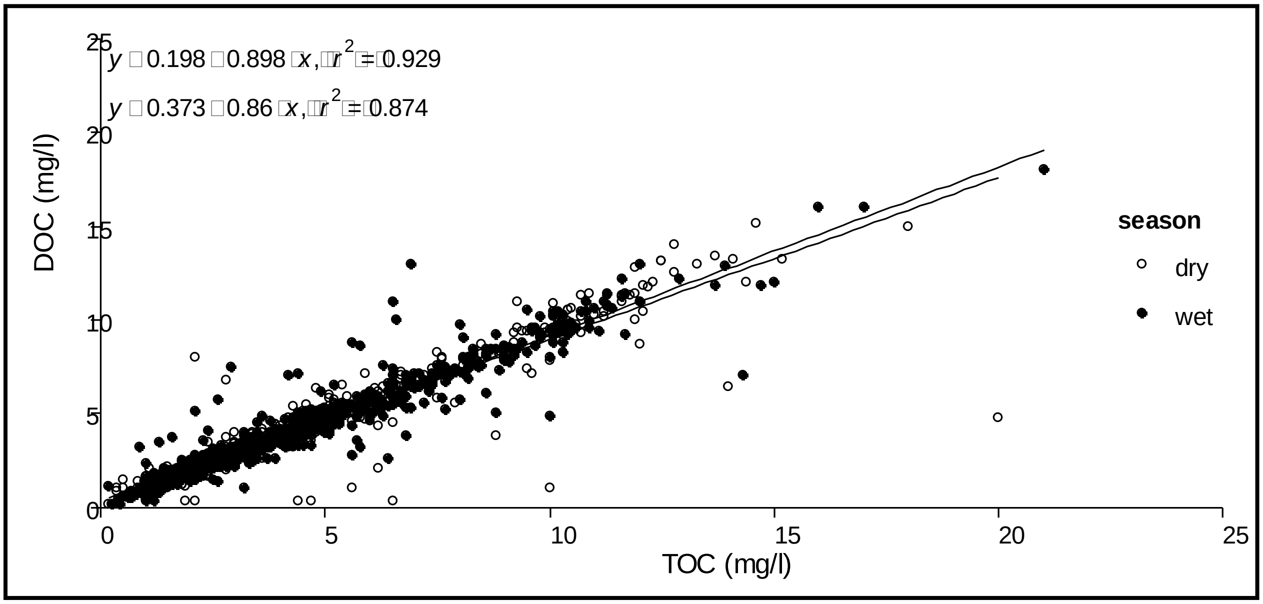
Figure 12: Measured vs. Predicted DOC calculated using regional translators



Seasonal differences in DOC concentration are expected as increased precipitation in the winter wet season, and snowmelt or low flow conditions in the summer dry season, are expected to affect DOC concentration differently (see section V.C.3.d for working definitions of the dry and wet season in Oregon). DEQ examined the statewide relationship between TOC and DOC in wet versus dry season samples (**Figure 13**). Although there was apparently a slight difference in the regression coefficients between the wet (black) and dry (gray) season samples, there was not an apparent difference between the regression models for the wet or dry season data.

Figure 13: Relationships between TOC and DOC by season

Solid lines are regression lines for the equations shown at upper left. Lines and equations show the wet season (top) and dry season (bottom).



As some regions may experience different seasonal effects due to geography and climate, such as snow melt in high elevation regions and low flow conditions in arid regions, we also examined the relationship between TOC and DOC in each region by season (**Figure 14**). Although regression coefficients appeared slightly lower in most regions, only samples in the Coastal region appeared to have a significant difference in the relationship between TOC and DOC in the wet and dry season (**Table 13)**, with an apparently much lower slope (0.26) during the dry season than other locations.

Figure 14: Relationships between TOC and DOC by region and season

Regression lines are shown as solid lines.

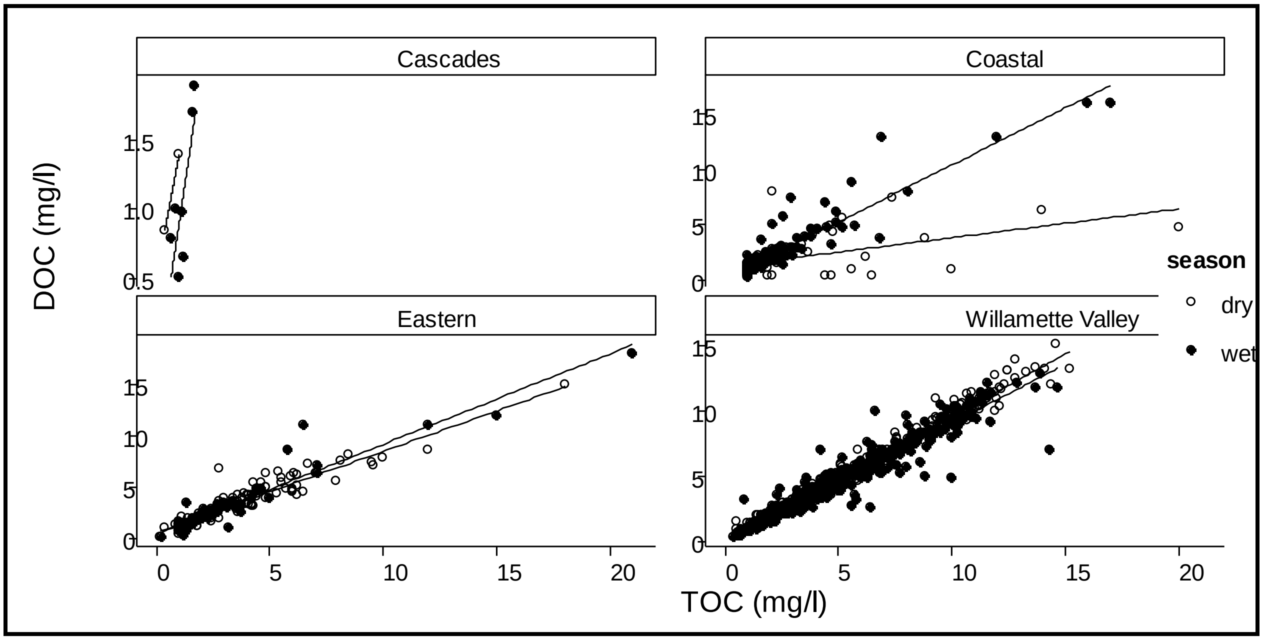
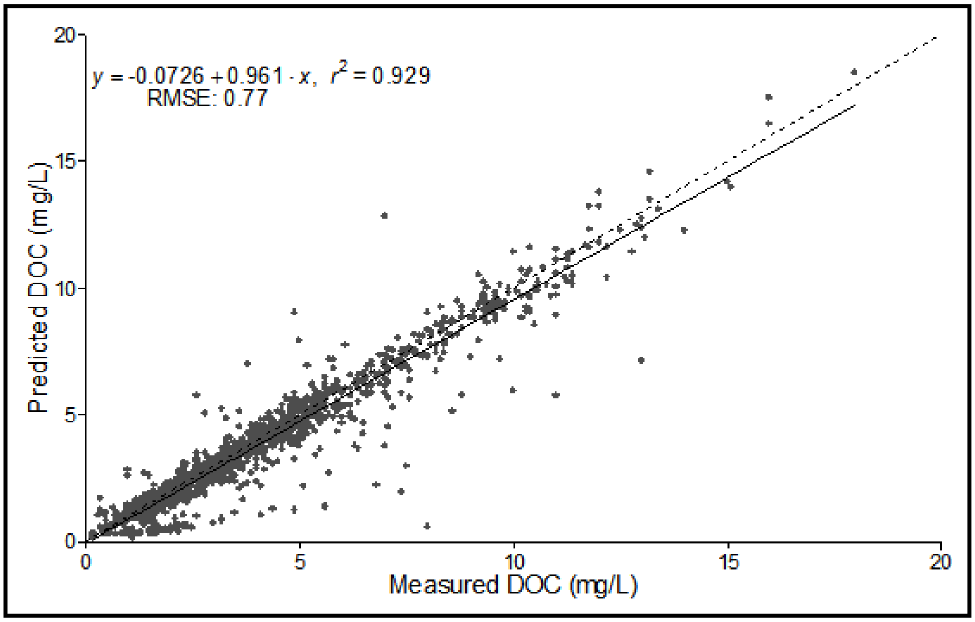


Table 13: Regression coefficients and R^2 values for TOC and DOC by region and season

Region	Season	TOC Regression Coefficient	Intercept	adj. R2
Cascades	dry	0.87	0.53	1
Cascades	wet	1.11	-0.21	0.649
Coastal	dry	0.26	1.25	.268
Coastal	wet	1.03	0.15	.862
Eastern	dry	0.79	0.62	0.891
Eastern	wet	0.88	0.38	0.909
Willamette Valley	dry	0.96	0.13	0.946
Willamette Valley	wet	0.90	0.05	0.981

Predicting DOC using ratio(s) of the regression coefficients from paired TOC:DOC data in **Table 13** at the appropriate temporal or spatial scale combinations of region × season slightly improved accuracy in modeled DOC concentrations (**Figure 13**). There was an incremental improvement in the adjusted R^2, to 0.92, and a small reduction in the root mean square error to 0.77 mg/L.

Figure 15: Measured vs. Predicted DOC calculated using regional and seasonal translators



The coefficient of regression relationships were between 0.83 and 1 for samples where there were sufficient TOC and DOC data to produce a reasonably accurate regression model (**Table 12,Table 13**). Although using regional, seasonal, and combined region × season regression coefficients as translators slightly improved the accuracy of predictions of DOC from TOC, there is high uncertainty in the accuracy of these coefficients for the Coastal and Cascade regions due to small sample size and high variability in the data.

DOC concentration]is generally a high ratio of 80%-100% of TOC concentration in the majority of our samples. Since DOC is a required BLM parameter, and the number of usable samples for calculating criteria is currently most limited by the availability of DOC data, DEQ applied the statewide conversion factor[49] of 0.83 to TOC data to estimate the expected DOC concentration for samples where DOC was not available. For samples where DOC > TOC, DEQ applied the same conversion factor to TOC to estimate DOC. We expect when the DOC > TOC it is due to measurement error or contamination of the DOC sample. Contamination of filters with organic matter and trace metals is an ongoing quality control issue for both DOC and copper analysis, and contributes to error in determining relationship between total and dissolved measurements of these parameters. This approach is conservative, as the IWQC will decrease with lower DOC concentrations with all else being equal.

[49] The conversion factor is based on the regression coefficient of 0.83. The TOC concentration is multiplied by this factor to approximate DOC (i.e. DOC = 0.83 * TOC).

V.C Data Description

V.C.1 Parameter Sensitivity

DEQ performed a sensitivity analysis on the BLM parameters in order to determine which parameters should be measured using field or lab analysis, and which parameters may be estimated to minimize uncertainty in BLM IWQC determinations for samples that may lack one or more required parameters. Using data from the Complete Measured Database DEQ applied a “one at a time” sensitivity analysis method adapted from an evaluation of fixed monitoring benchmarks in Colorado by EPA Region 8 and the state of Colorado[50], and an evaluation of potential water quality criteria for Oregon by Tobiason, DeForest, and others.[51]

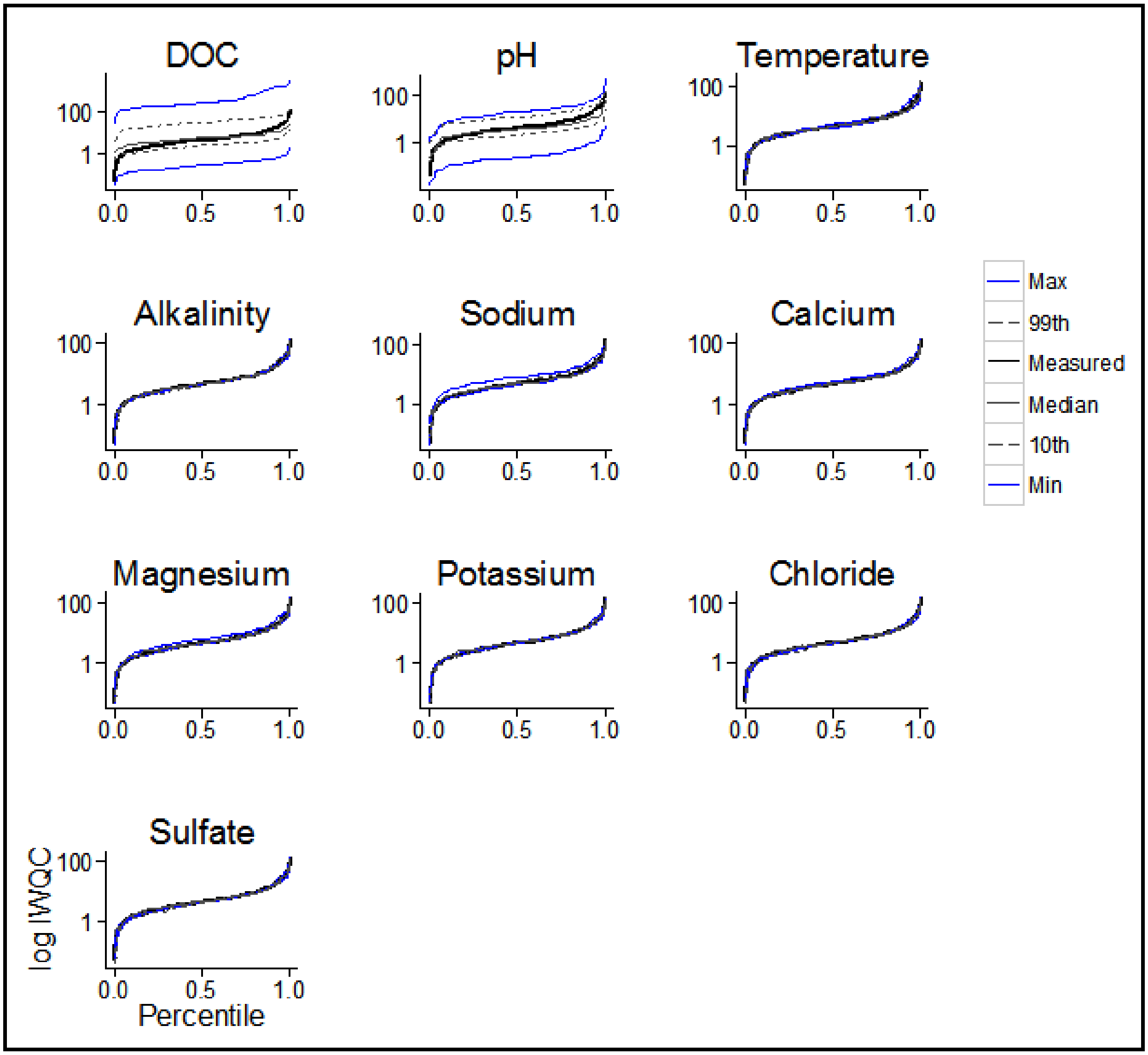
1. DEQ compiled a table of summary statistics, including the maximum, 99th percentile, median, 10th percentile, and minimum value of all available BLM parameter data.
2. DEQ calculated BLM IWQC for all samples from the complete sets of measured BLM input parameters (see **Figure 18**, **Figure 17**, **Table 15**, **Table 16**).
3. For each BLM parameter, the measured values in each sample were substituted one at a time with the maximum, 99th percentile, median, 10th percentile and minimum value of the parameter, then BLM IWQC were generated for each sample in the data set. A total of 2,166 permutations were generated.

A graph of the IWQC from each substitution for each parameter is shown in **Figure 16**. Parameters with a high sensitivity in the model, such as DOC and pH, show large deviations between IWQC based on measured values versus IWQC based on the substituted values. Parameters with low sensitivity, such as Ca, show small deviations between IWQC calculated from measured values and substituted values. The significance of the deviations, such as max, min, and various percentiles, is shown by the relative spacing between the curve of measured values and the curves of the various substituted values.

[50] EPA (2012). Calculation of Fixed Monitoring Benchmarks for Copper at Selected Monitoring Sites in Colorado. Office of Water, United States Environmental Protection Agency. **4304T**.

[51] Tobiason, S., D. DeForest, N. Lewis and R. Gensemer (2014). Potential Water Quality Criteria for Copper in Oregon State Fresh Waters based on the Biotic Ligand Model. SETAC Annual Meeting, Vancouver, British Columbia, Canada.

Figure 16: Sensitivity of IWQC to substitution of BLM parameters



The results of the sensitivity analysis show that the BLM is particularly sensitive to changes in DOC, pH, and to some extent extremely high Na^{+} concentrations. These findings are generally consistent with Hydroqual 2008[52] and EPA 2012[53]. Therefore:

- Measured values for DOC and pH values should be used when generating BLM IWQC.
- Using specific conductance measurements is an accurate method to estimate missing geochemical ions, especially sodium, which is a relatively sensitive BLM parameter.

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[52] HydroQual (2008). Calculation of BLM Fixed Monitoring Benchmarks for Copper at Selected Monitoring Sites in Colorado, Final Report. HydroQual,Inc. October 10, 2008.

[53] EPA (2012). Calculation of Fixed Monitoring Benchmarks for Copper at Selected Monitoring Sites in Colorado. Office of Water, United States Environmental Protection Agency. **4304T**.

- For less-sensitive parameters, any errors introduced by the estimation of missing values for geochemical ions and alkalinity using either regional medians of existing data, or correlation to specific conductance data (see section VI.A.1) are unlikely to have a significant influence on the estimation of the distribution for IWQC.

This suggests that the Complete Measured Database can be expanded to include samples where estimates of one or more BLM parameters (other than pH and DOC) are unlikely to impact BLM IWQC outcomes (**Table 14**). Given the results of the sensitivity analysis, this would allow for generating accurate BLM IWQC using estimates of missing geochemical ions and alkalinity data.

Table 14: Size of potential data sets based on most-sensitive BLM parameters

Parameter	Sample size	Importance:
pH	20,827	Highly sensitive BLM parameter. Potentially limits the number of samples for calculating BLM criteria.
DOC	4,992	Highly sensitive BLM parameter. Limits the number of samples usable for calculating BLM criteria.
Specific conductance	21,504	Estimator of missing geochemical cations and anions for “gaps” in samples.
Copper	4,169	Component of FMB, Toxic Units, or compliance evaluation. Limits the number of samples available for FMB calculations and for evaluating compliance with IWQC.
Hardness	1,957	For comparison of BLM IWQC with the existing hardness-based criteria
Estimated Usable Samples	4,607	Samples with a combination of at least DOC, pH and specific conductance data.

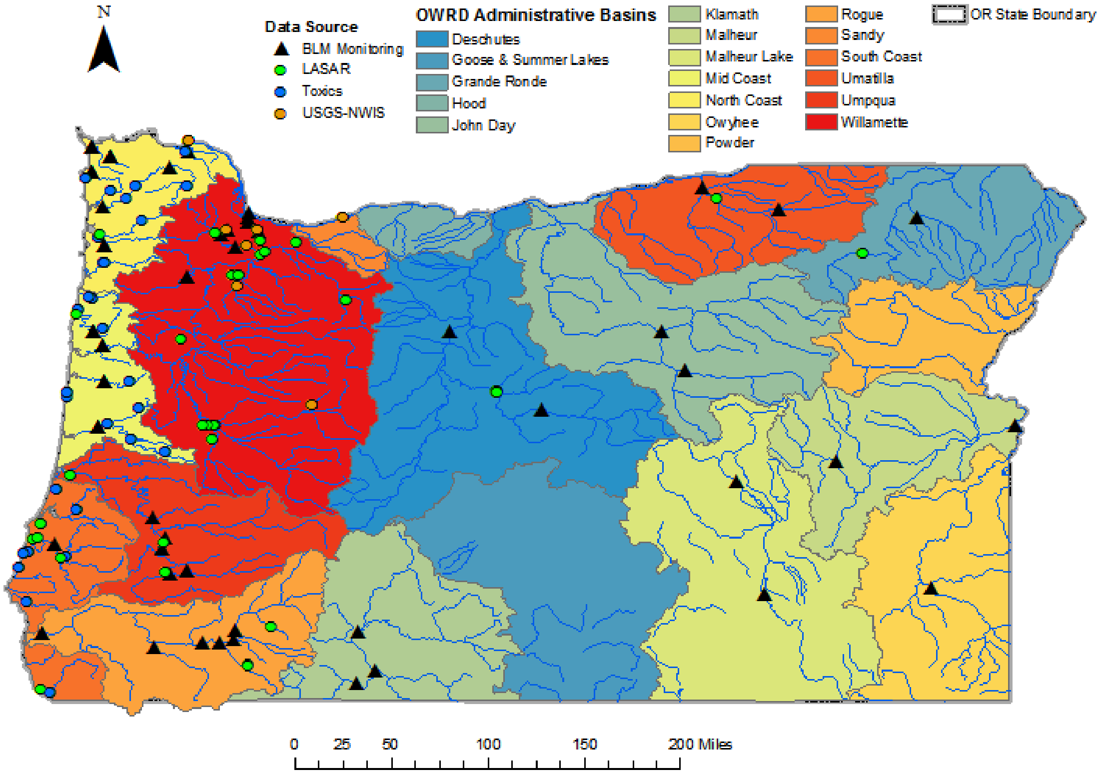
V.C.2 Data Completeness

As indicated in section V.A., the initial Oregon BLM database contains data from 823 locations, with over 155,000 individual measured results for BLM criteria derivation. Only a small set of samples have concurrent measurements for all 10 measured BLM input parameters made at the same date and location. Accordingly, there are 164 sites containing at least one sample where all values of BLM parameters are measured (**Table 15**, **Figure 17**). Complete samples are more frequently from sites in the Coastal basins, where many threatened and endangered salmonid populations are located, and the Willamette Valley basin, where a majority of permitted discharges are located. There are only four sites representing the relatively undisturbed basins in the Cascades basins of Hood and Sandy.

Table 15: Number of sites with all BLM parameters

OWRD Basin	sites (n=)
Deschutes	7
Grande Ronde	4
Hood	1
John Day	2
Klamath	3
Malheur	2
Malheur Lake	2
Mid Coast	17
North Coast	28
Owyhee	1
Powder	1
Rogue	11
Sandy	2
South Coast	22
Umatilla	4
Umpqua	10
Willamette	47
Total Sites	**164**

Figure 17: Location of sites with complete sets of samples within Oregon Water Resources Department (OWRD) administrative basins.



The 164 sites with complete values for all BLM input parameters provide a total of 361 samples (**Table 16**). These samples were subset into a database of complete BLM samples for evaluating model parameter sensitivity and methods to estimate missing parameters. Hereafter, this data set is referred to as the Complete Measured Database. Using this database (n=361), BLM IWQC outcomes can be compared between measured and estimated values of each BLM parameter. DEQ utilized this database of complete BLM samples to evaluate estimation methods for missing parameters in section V.C.2. A table of the site identities and summary of the samples is in Appendix A.

Table 16: Number of complete sets of BLM samples per region and per season

By OWRD Basin	Sample size
Deschutes	13
Grande Ronde	6
Hood	2
John Day	4
Klamath	5
Malheur	4
Malheur Lake	4
Mid Coast	39
North Coast	103
Owyhee	2
Powder	2
Rogue	14
Sandy	8
South Coast	32
Umatilla	6
Umpqua	16
Willamette	102
Total	**361**
By Season	**Sample size**
Wet	220
Dry	141
Total	**361**

V.C.3 Seasonal Representation

There is adequate representation of samples from both wet and dry seasonal periods. The number of monthly samples are generally even throughout the year. These ranged from 149-320 sites sampled per month (**Figure 18**).

The number of samples was relatively equal between the wet season and dry season, with about 20% more samples made during the dry season. The months where a majority of the precipitation occurs defines the wet season. The wet season is the period between October 1 and May 31, when rain events are frequent and Oregon receives on average 88% of its annual precipitation. The dry season is the period from June 1 to September 30, when precipitation events are smaller and less frequent. The number of monthly samples are generally even within seasons, with about 20% more samples made during the dry season (**Figure 18**). The number of sites sampled per month ranged from 149-320, with more samples collected during the warmer months May-October, when precipitation is less frequent and flows tend to be lower (**Table 17**).

Figure 18: Number of parameter samples collected per month

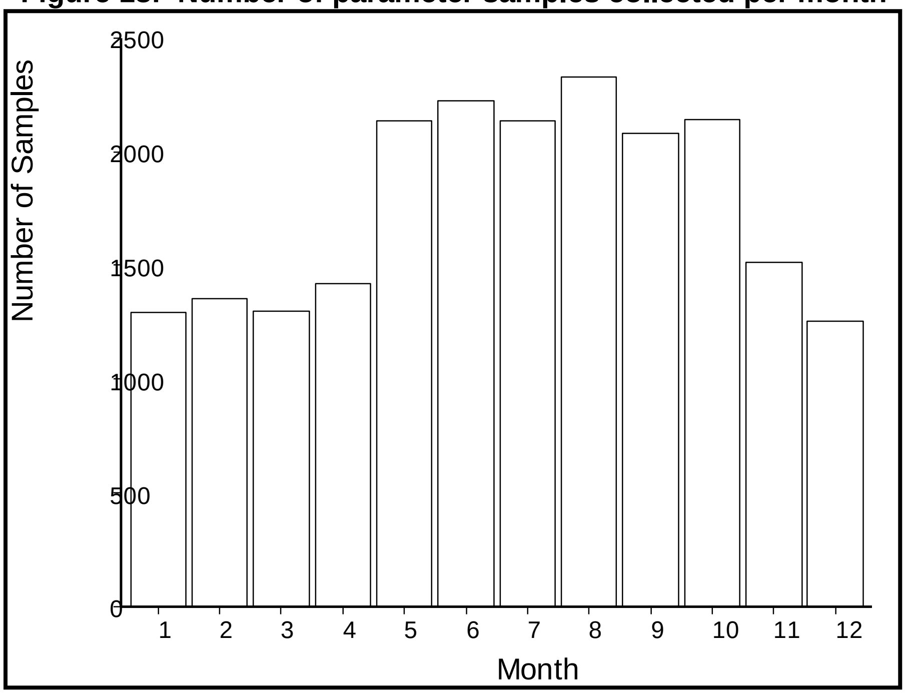


Table 17: Sites sampled per month

Month	Sites Sampled (n)
January	168
February	149
March	198
April	187
May	279
June	231
July	270
August	320
September	277
October	257
November	233
December	168
Total Wet Season	**465**
Total Dry Season	**553**

VI. Evaluation of Data Estimation Methods

VI.A Estimating Missing Parameters

The number of samples in the Oregon database where BLM criteria can be calculated from samples with a complete set of the BLM parameters is limited to 361 samples at 164 locations. The EPA anticipates that many users will not necessarily have access to measured data for all BLM parameters, and is in the process of developing approaches to estimate some of the missing water quality parameters for the BLM. EPA does not expect official release of this document, *Development of Tools to Estimate Water Quality Parameters for the Biotic Ligand Model* until 2016.[54] This document, hereafter referred to as EPA's Missing Parameters document, presents two approaches for closing data gaps for missing BLM parameters. These two methods estimate model inputs for missing BLM parameters that are based on a nationwide set of water quality data.

[54] EPA (2012). Development of Tools to Estimate Water Quality Parameters for the Biotic Ligand Model. Office of Water. April 2012. **820R12008.**

EPA Estimation Methods:

1. A linear regression approach based on the correlation between geochemical ions and specific conductance. Specific equations are provided to estimate the geochemical ions for samples where specific conductance data are available. Section VI.A.1 duplicates the derivation of this approach using the Oregon dataset.

2. A geostatistical approach based on interpolating concentrations for unmeasured locations by kriging[55] between sampling sites that have measured parameter data. Means and percentiles are provided for use as default parameter values. Specific 10th percentile values are provided in the EPA document for each Level III Ecoregion in the U.S., nine of which are in Oregon. Section VI.B evaluates the median and percentiles grouped by Ecoregion and other geographic schemes, without kriging, with data from the Oregon dataset, and contrasts them with the EPA estimates.

EPA evaluated these approaches at the continental U.S. scale using a nationwide dataset of archived data from the USGS-NWIS database and the EPA Wadeable Streams Assessment. In section VI.B, DEQ compared the range of IWQC values calculated from Level-III Ecoregional estimates of DOC using data from EPA to DEQ Ecoregional and BLM physiographic region estimates for DOC to actual IWQC values calculated from the Complete Measured Database.

VI.A.1 Correlation of Cations and Anions with Specific Conductance

The concentrations of many water quality parameters co-vary with one another to varying degrees based on the underlying geochemistry of any given area. One of the estimation techniques suggested by the USGS was to use the high correlation between many geochemical ions and specific conductance in order to estimate the value of these ions. Specific conductance, a 25°C temperature-normalized measure of electrical conductivity, is an inexpensive and widely collected constituent of water quality, with units commonly provided in µmhos/cm (these units are the inverse of the resistivity unit (ohm) and are also known as µSiemens/cm or simply µS/cm). The Oregon BLM dataset has over 22,000 samples that contain specific conductance data, many of them missing just one or a few more of the geochemical ions and alkalinity.

DEQ assessed the relationship between the BLM input parameters and specific conductance using a combination of correlation analysis to identify strong relationships, and linear regression to derive equations for estimating certain BLM parameters.

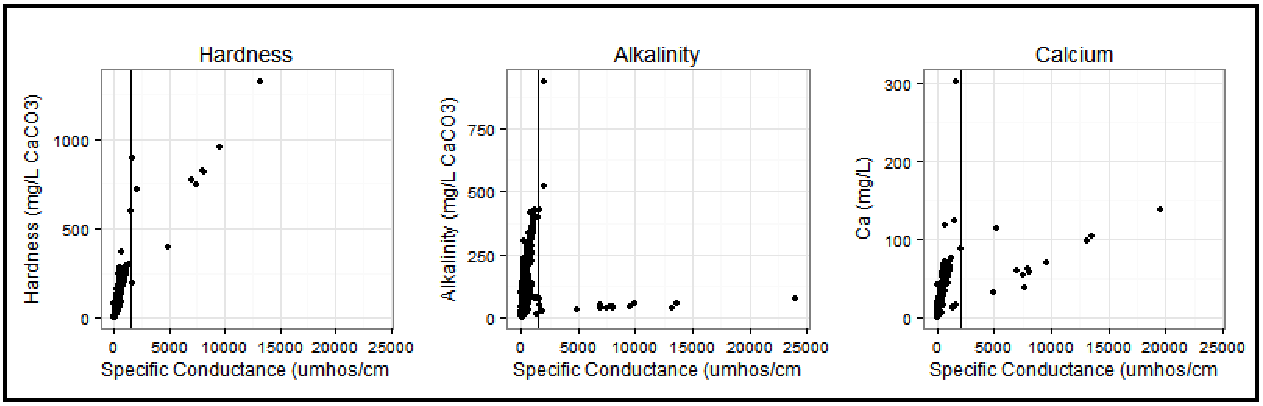
DEQ did not include samples with specific conductance measurements of more than 1500µmhos/cm because our objective was to apply the BLM to fresh, surface waters. Standard conductivity ranges for rivers in the United States is 500-1500 µmhos/cm, with conductivity above 2000 µmhos/cm typical in

[55] "Kriging" is a statistical method used to estimate the values of a process between points using data from points where samples are collected. Kriging estimates the value between points by modeling the covariance structure of sampled locations to provide a best linear unbiased prediction of intermediate values.

marine waters.[56] The 1500 µmhos/cm threshold provides a useful screening tool for anomalous data collected from potentially contaminated or marine influenced sites as indicated by relatively high specific conductance. However, this threshold may not necessarily screen all samples of groundwater, or those potentially contaminated by leachate, or effluent, or other confounding sources. Samples with specific conductance greater than 1500µmhos/cm exhibited results for geochemical ions that had markedly different relationships with conductivity than other samples (i.e. results to the right of solid vertical reference lines in **Figure 19**).

Figure 19: Relationships between specific conductance and select geochemical parameters.

Vertical reference line is specific conductance at 1500 µmhos/cm.



The results of the correlation analysis for the Oregon BLM Database are shown in **Table 18**. DEQ used Spearman's rank correlation (ρ), a non-parametric method of statistical dependence. Values approaching +/- 1 indicate a strong positive/negative correlation between the relative value of a variable and the value of specific conductance in the sample, while a value of zero indicates no relationship between the relative values. This method is robust when data are not normally distributed or for non-linear relationships. There was a poor correlation between specific conductance and DOC ($\rho = 0.599$) and pH ($\rho = 0.088$). There was strong positive correlation, ranging from 0.81- 0.97, between specific conductance and the geochemical ions, alkalinity and hardness. These correlation coefficients are comparable to those found in EPA's Missing Parameters document using pooled samples collected from Colorado, Utah and Wyoming. The EPA limited their regression analysis to the lower 10th percentile of their data to provide a conservative estimate and to reduce the amount of variability in their data. Their analysis was not intended to provide an accurate estimate of geochemical ion concentration, and would not accurately predict ion concentrations over the full range of ion concentrations in the environment.

[56] APHA. 1992. *Standard methods for the examination of water and wastewater.* 18th ed. American Public Health Association, Washington, DC.

Table 18: Correlation of BLM Parameters with specific conductance

Parameter	Spearman's ρ	
	OR-DEQ	EPA, 2012
DOC	0.599*	0.866
pH	0.088*	0.175
Alkalinity	0.894*	-0.600[57]
Hardness	0.973*	N/A
Ca	0.959*	0.867*
Na	0.899*	0.921*
Mg	0.945*	0.882*
K	0.819*	0.846*
Cl	0.890*	0.827*
Sulfate	0.889*	0.905*
* = p<0.001; Correlation on median value at each site		

The correlation analysis suggests potential for strong regression relationships between specific conductance and the geochemical ions and alkalinity.

Figure 20 shows scatter plots of log-transformed specific conductance versus BLM parameter concentration. The color of the points indicates the data source where DEQ acquired the samples. The dashed line in each plot is the best-fit line of an ordinary least-square regression. DEQ conducted a series of linear and logarithmic OLS regressions on the full dataset and a subset of the 10th percentiles of the data (see **Table 19**).

[57] This value is expected to be corrected in the final version of the EPA Estimation of Missing Parameters document as an error. The correlation coefficient between alkalinity and specific conductance should be comparable to the other geochemical ions (Doug Endicott, Great Lakes Environmental Center. Personal communication, May 14, 2014.)

Figure 20: Relationships between specific conductance and BLM input parameters

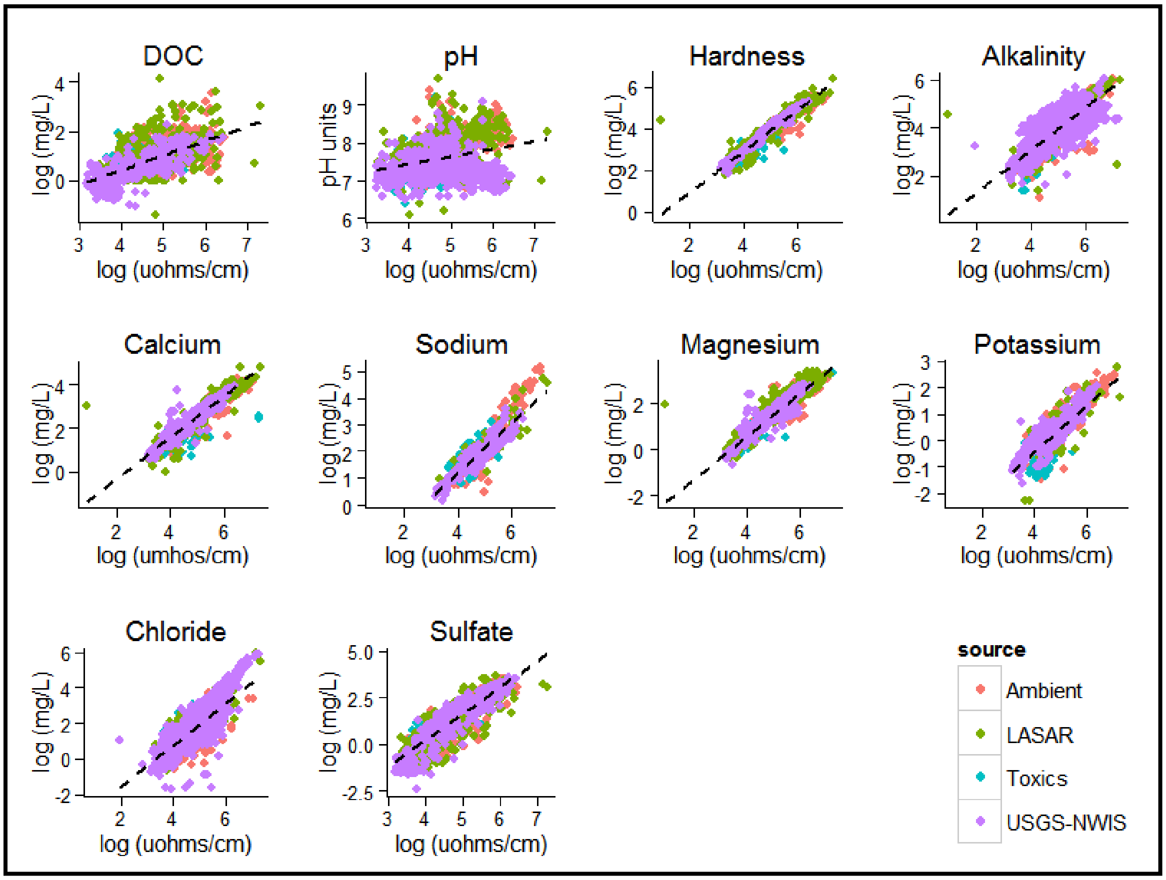


Table 19: Goodness of fit for specific conductance.

Best-fit models for each parameter are shown highlighted.

Adjusted R^2 of least-squares linear regression against specific conductance				
	Regression Type			
	Linear	Linear	Natural Log	Natural Log
Parameter	All Data	10^{th} Percentile	All Data	10^{th} Percentile
DOC	0.13	0.04	0.31	-0.0007
pH	0.049	0.002	0.03	0.001
Hardness	0.92	0.25	0.92	0.26
Alkalinity	0.65	0.31	0.77	0.29
Calcium	0.87	0.40	0.89	0.39
Sodium	0.62	0.28	0.82	0.30
Magnesium	0.74	0.67	0.85	0.69
Potassium	0.69	0.23	0.70	0.21
Chloride	0.63	0.59	0.77	0.56
Sulfate	0.60	0.003	0.76	0.0005

EPA's Missing Parameters document did not include R-squared or similar goodness of fit information for the specific conductance regressions in their draft report. EPA's Missing Parameters document did indicate that all correlations were significant to $p<0.001$. The EPA regressions were limited to the 10^{th} percentile of water quality data from Colorado, Utah and Wyoming because it provided a conservative estimate of the parameters and reduced the high variation observed for data in these three states. DEQ found significant regression relationships for log-transformed parameters over the entire range of Oregon data, except pH, which was not evaluated due to the absence of a significant correlation. Although the regression equation was significant for DOC (p=0.599 in **Table 18**), the R^2 for DOC indicated a relatively poor fit. R^2 values for geochemical ions, alkalinity and hardness ranged from 0.70-0.92.

Using the regression equations for calculating parameter concentration based on specific conductance shown in **Table 20**, DEQ re-calculated the concentration for each parameter in the set of complete samples used for sensitivity analysis in section V.C.1. DEQ then calculated the IWQC for these samples and compared them to the IWQC for the same samples with completely measured parameters.

Table 20: Specific conductance regression equations for Oregon data

Parameter	Regression Equation	Adjusted R^2	p-value
DOC	$\ln(y) = 0.69 \cdot \ln(x) – 2.43$	0.31	< 0.001
Hardness	$\ln(y) = 1.02 \cdot \ln(x) – 1.16$	0.92	< 0.001
Alkalinity	$\ln(y) = 0.88 \cdot \ln(x) – 0.41$	0.77	< 0.001
Calcium	$\ln(y) = 0.96 \cdot \ln(x) – 2.29$	0.89	< 0.001
Sodium	$\ln(y) = 0.86 \cdot \ln(x) – 2.22$	0.82	< 0.001
Magnesium	$\ln(y) = 0.91 \cdot \ln(x) – 3.09$	0.85	< 0.001
Potassium	$\ln(y) = 0.84 \cdot \ln(x) – 3.74$	0.70	< 0.001
Chloride	$\ln(y) = 01.15 \cdot \ln(x) – 3.82$	0.77	< 0.001
Sulfate	$\ln(y)= 1.45 \cdot \ln(x) – 5.59$	0.76	< 0.001

Since chronic criteria are generally more conservative than acute criteria, and are more likely to determine compliance with copper water quality criteria in Oregon, DEQ focused on the chronic criteria generated by the BLM. Stepwise comparison of chronic BLM copper IWQC generated using measured parameters (x-axis) to IWQC generated from one-at-a-time substitution of parameters estimated from the regression on specific conductance equations (y-axis) is shown in **Figure 21**. The y-axis of each panel shows the concentration of the parameter indicated as substituted by values calculated using the regression equations from **Table 20**. In each panel, the y-axis indicate the BLM input parameter being substituted, while all other model parameters are held constant at their measured values. The dashed line is a 1:1 line where IWQC from samples with an estimated parameter would be equal to the IWQC for all measured parameters. Substituting the concentration of DOC with values calculated from the specific conductance regression equation had poor agreement with measured IWQC as can be seen by the relatively high dispersion around the 1:1 line in the upper left plot of **Figure 21**. The concentration of each of the geochemical ions and alkalinity showed good agreement between data sets for calculated and measured IWQC. **Figure** 22 shows the relationship between chronic (CCC) IWQC by estimating all geochemical ions and alkalinity simultaneously using the **Table 20** specific conductance regression relationships. The dashed line is a 1:1 line, and the results of an OLS regression and the root mean square error of estimates is at the upper left. Because the root mean square error of the estimation is very low (0.53 µg/L, or about half of the typical analytical detection limit for Cu in our database), the analysis shows that IWQC can be reliably estimated from samples where data for geochemical ions and alkalinity are missing.

Figure 21: Observed versus estimated IWQCs by regression on specific conductance, per parameter

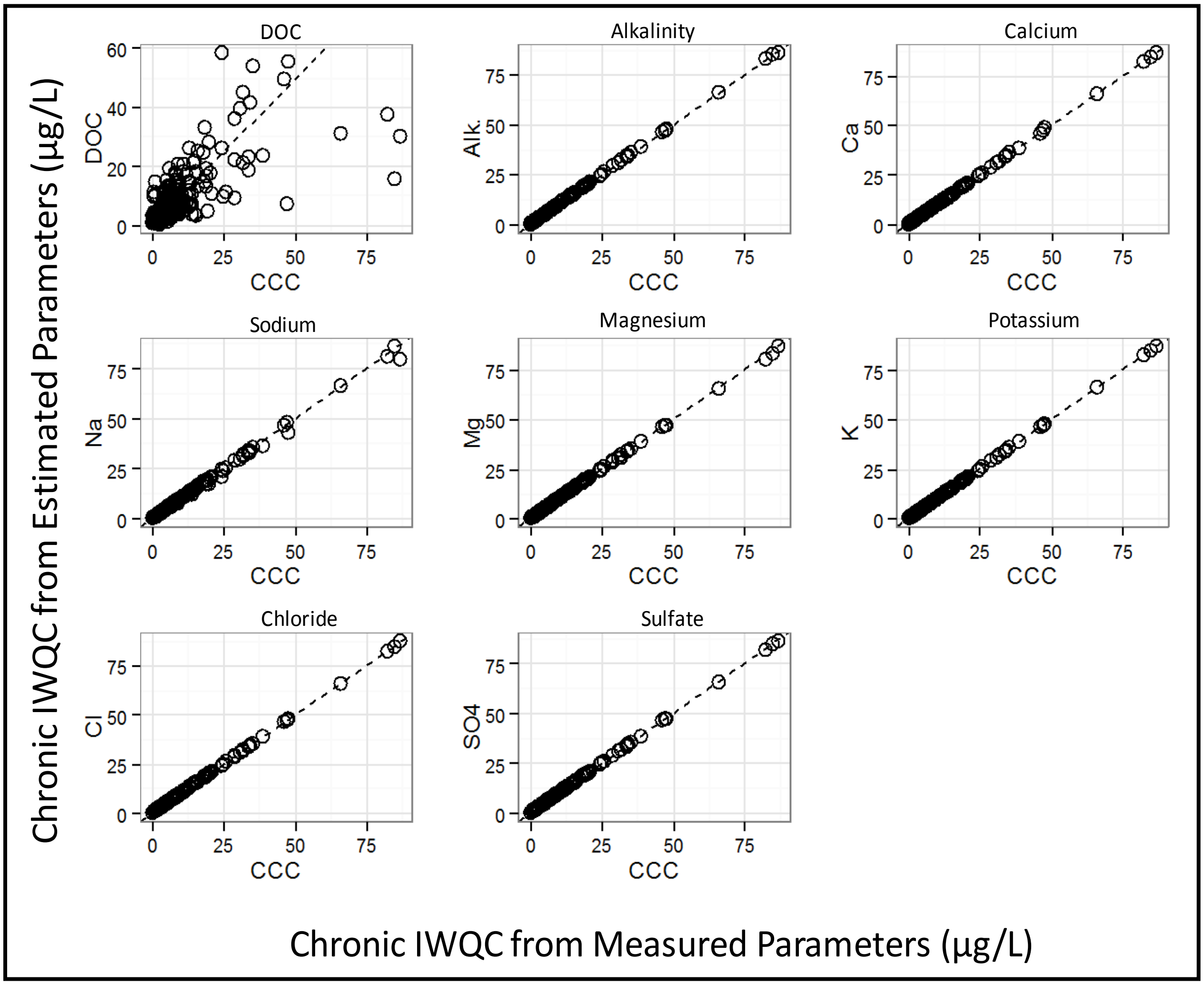
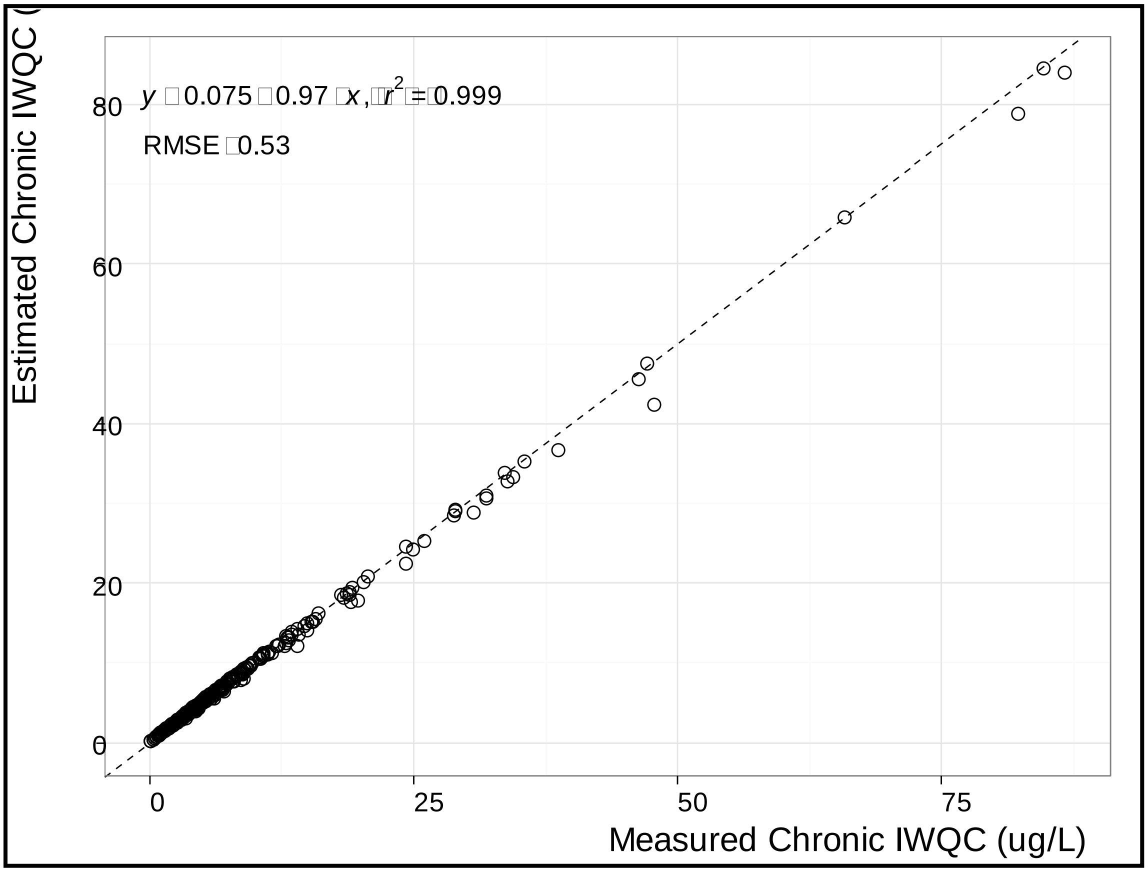


Figure 22: Observed versus estimated IWQC with estimates by regression on specific conductance for all BLM parameters other than DOC, pH and temperature



Given the poor correlation of DOC and pH with specific conductance, and the sensitivity of the BLM model to these parameters, measured values of these parameters are the only reliable method for accurate calculation of BLM IWQC. DEQ did not conduct regression analysis between specific conductance and temperature because we did not expect any environmentally relevant relationship between these parameters. Temperature is a commonly measured parameter, and has a low effect on BLM IWQC calculations (**Figure 20**). Little error would be introduced by using estimated temperature values. On a case by case basis, users may be able to estimate temperature based on nearby temperature monitoring sites or use an assumed temperature value when temperature data are missing.

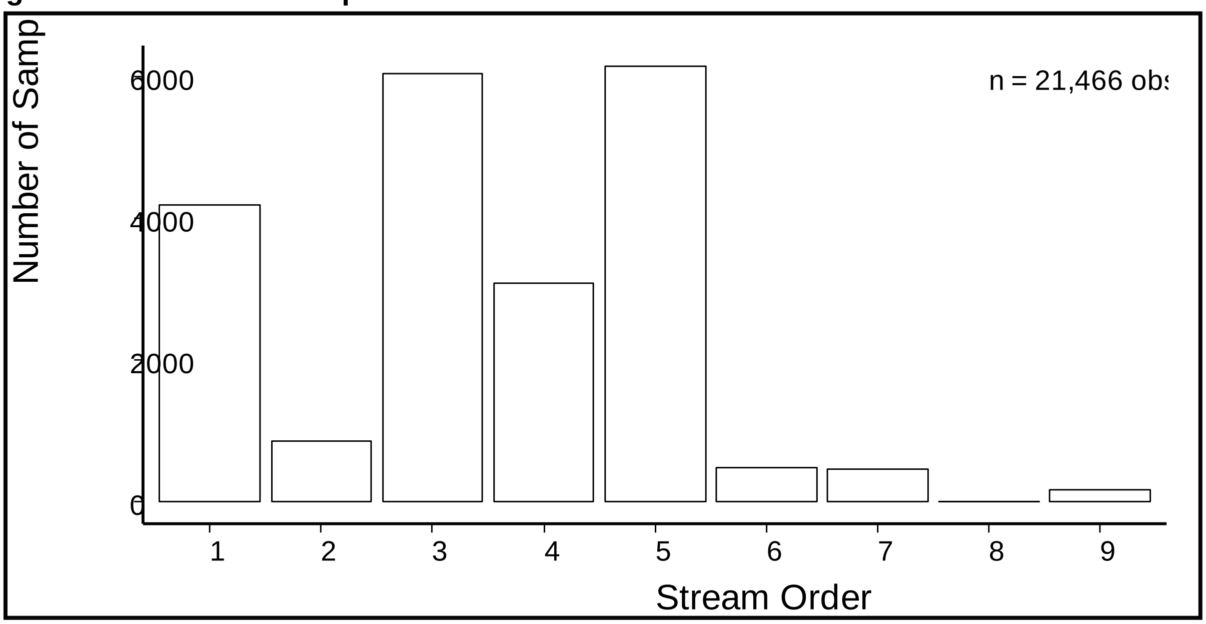
VI.A.2 Stream-order Specific Conductance Estimation Methods

EPA is expected to include stream order as a factor in the method they recommend for estimating missing BLM parameters as part of its update to the *Tools to Estimate Water Quality Parameters for the Biotic Ligand Model*[58] document, hereafter referred to as EPA's Missing Parameter document. Stream order is a

[58] EPA (2012). Development of Tools to Estimate Water Quality Parameters for the Biotic Ligand Model. Office of Water. April 2012. **820R12008.**

method of numbering streams hierarchically within a network. The smallest un-branched tributary is a first-order stream, the stream receiving the tributary is a second-order stream, and so on, with the main stream always of the highest order. Classification of reaches by stream order tends to separate steeper gradient, lower discharge, and potentially less impacted headwater and low-order tributary streams from high-order, high discharge, low gradient and potentially impacted streams, such as valley bottoms and larger tributaries likely to serve as receiving waters for discharges. Stratifying specific conductance data by stream order is expected to provide more accurate estimates of stream conditions by developing regression relationships among streams of similar discharge and biogeochemistry. Stratifying the prior analysis by stream order may provide a means to reduce variability in DOC, pH and geochemical ion parameters if they tend to differ between headwater streams and larger receiving waters. DEQ investigated the potential of using stratification by stream order as a method to improve the ability to estimate missing geochemical ions. DEQ also investigated the potential for stratification by stream order to improve the correlation of DOC or pH with specific conductance.

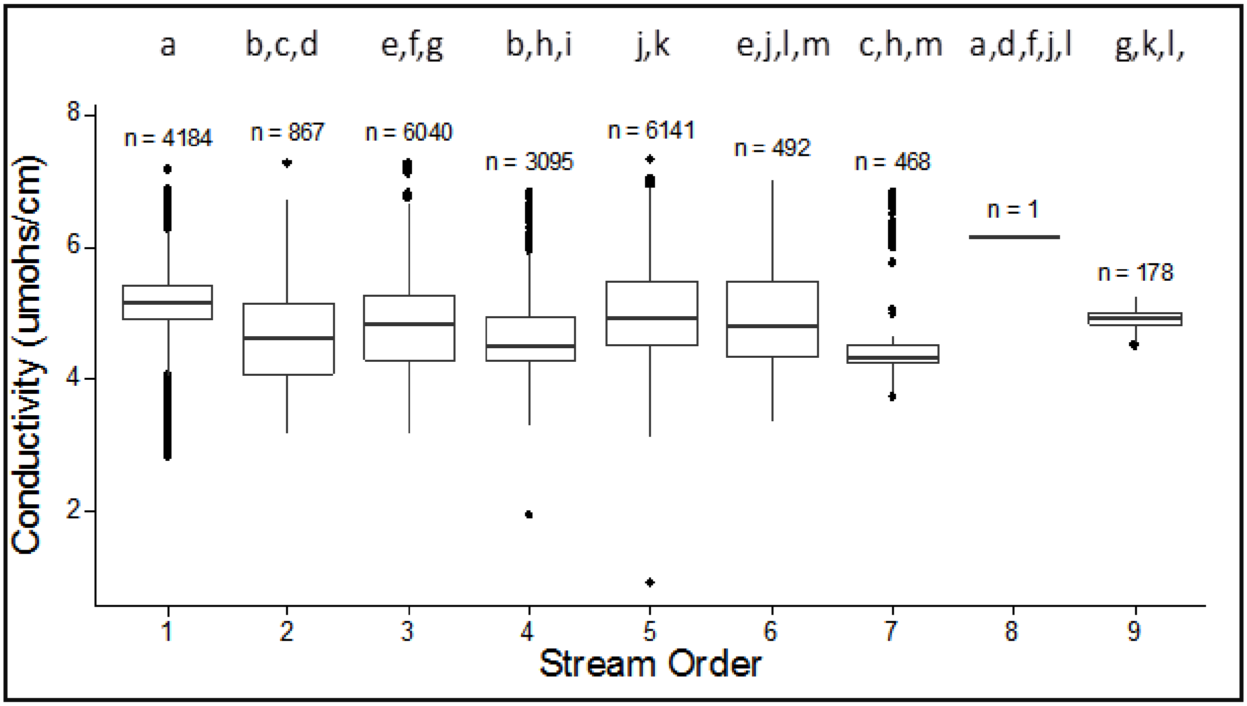
Figure 23: Number of samples in stream-order and stream-order classes



The Strahler stream order for the reach where each sample site was located was obtained by GIS overlay of site locations with data from the National Hydrography Dataset (NHD)[59]. Samples in the Oregon database are frequently in headwater streams of low order (1-2) and mid-size tributaries and minor rivers of moderate to high order (3 and 5). For comparison, the Willamette River at Portland is a 6th order stream.

[59] National Hydrography Dataset, version 2, U.S. Geological Survey (USGS). http://nhd.usgs.gov/data.html Accessed 07/20/2015.

Figure 24: Distribution of specific conductance data among stream orders



The distribution of specific conductance data showed patterns of relatively high variability for smaller order streams (Order 1-6), and somewhat lower variability than various sites on higher-order reaches of the Columbia River (Order 7-9) (**Figure 24**).

DEQ used an ordinary least-squares (OLS) multi-linear regression approach to model each parameter as a function of specific conductance and stream order. The results of this analysis are shown in **Table 21**. Goodness of fit was evaluated using the adjusted R^2 value to account for the number of parameters in each regression model. We accounted for the effect of the additional stream order covariate by using the Akiake Information Criteria (AIC). The AIC evaluates the goodness of fit of a model while also accounting for the tendency for the addition of covariates to increase R^2, regardless of the quality of the model. Therefore, DEQ could evaluate the relative quality of two models with different numbers of covariates by comparing their AIC criteria values. A lower AIC value represents a model with higher quality. For the geochemical ions, our results showed that using stream order as a covariate with specific conductance slightly increased the R^2 value over the **Table 20** regression equations for four parameters: alkalinity, sodium, sulfate, and hardness, which is not a BLM parameter, but is the basis of the copper standard currently in effect. In general, the AIC values for the models using stream order as a covariate with specific conductance were also slightly lower (improved) for all parameters except hardness, than for specific conductance alone.

DEQ also examined regression models for pH, DOC and Cu (**Table 22**). Neither copper nor pH had significant regression relationships to conductivity alone, and so we omitted both from **Table 20**. For DOC, there was not a marked improvement in either the R^2 or AIC for these parameters by adding stream order. Thus, specific conductance, alone or in combination with stream order, is not a useful surrogate for estimating these parameters.

Table 21: Multi-linear regression of geochemical ions by specific conductance and stream order

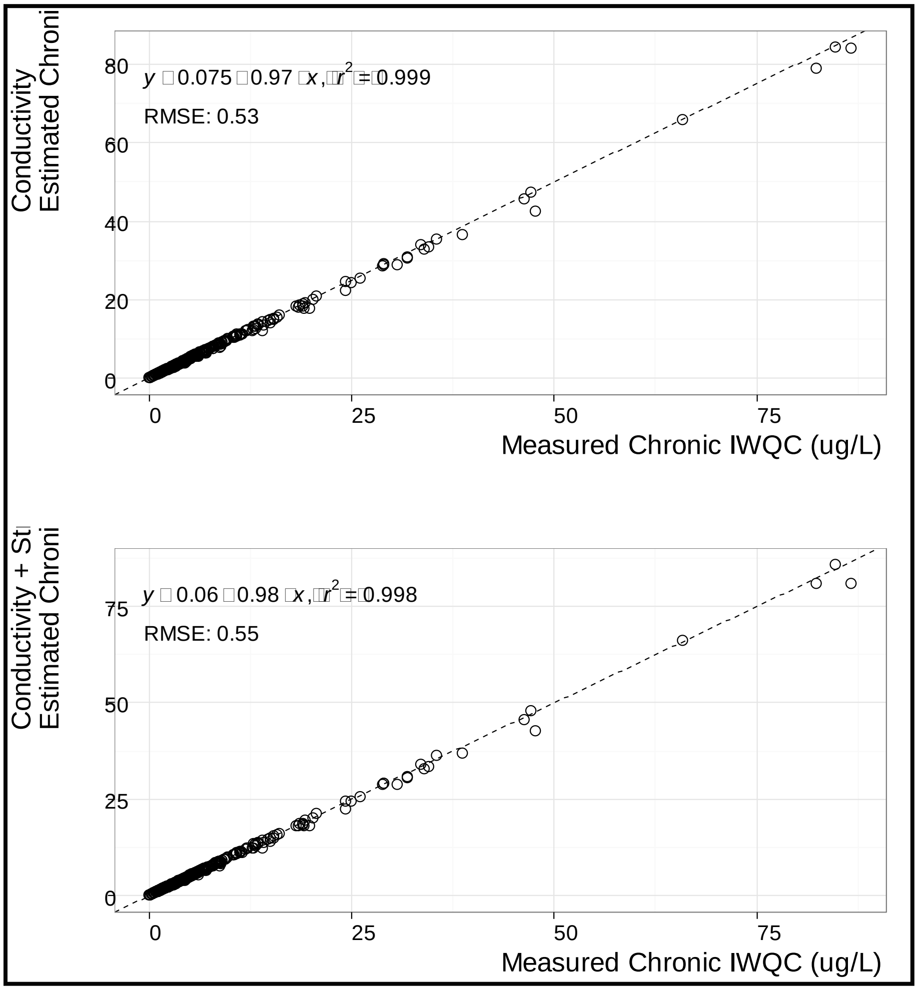
	Specific conductance			Specific conductance + Stream Order		
Parameter	Equation	R^2	AIC	Equation	R^2	AIC
Alkalinity	ln(A) = 0.88·ln(EC) – 0.41	0.77	3,736	ln(A) = 0.86·ln(EC) – 0.05 · ln (SO) – 0.14	0.80	2,000
Calcium	ln(Ca) = 0.96·ln(EC) –2.29	0.89	-1,111	ln(Ca) = 0.95·ln(EC) + 0.008 · ln (SO) – 2.23	0.89	-1,124
Hardness	ln(Ha) = 1.02·ln(EC) –1.16	0.92	-376	ln(Ha) = 0.984·ln(EC) + 0.015 · ln (SO) – 1.07	0.93	-411
Potassium	ln(K) = 0.86·ln(EC) –3.89	0.65	1,316	ln(K) = 0.87·ln(EC) – 0.03 · ln (SO) – 3.67	0.65	1,299
Magnesium	ln(Mg) = 0.91·ln(EC) –3.09	0.86	-178	ln(Mg) = 0.92ln(EC) – 0.02 · ln (SO) – 3.02	0.86	-270
Sodium	ln(Na) = 0.92·ln(EC) –2.47	0.83	512	ln(Na) = 0.92·ln(EC) – 0.02 · ln (SO) – 2.39	0.84	483
Chloride	ln(Cl) = 01.15·ln(EC) –3.82	0.77	12,292	ln(Cl) = 1.18·ln(EC) + 0.01 · ln (SO) – 4.01	0.77	12,165
Sulfate	$\ln(SO_4)$= 1.45·ln(EC) –5.59	0.76	3,212	ln(SO4) = 1.43·ln(EC) + 0.12· ln (SO) – 6.08	0.80	2,894

Table 22: Multi-linear regression of pH, DOC, and Cu by specific conductance and stream order

	Specific conductance			**Specific conductance + Stream Order**		
Parameter	**Equation**	**R^2**	**AIC**	**Equation**	**R^2**	**AIC**
pH	$\ln(pH) = 0.01 \cdot \ln(EC) + 1.94$	0.026	68,603	$\ln(pH) = 0.01 \cdot \ln(EC) - 0.002 \cdot \ln(Ord) + 1.93$	0.036	68,833
DOC	$\ln(DOC) = 0.69 \cdot \ln(EC) - 2.42$	0.31	10,319	$\ln(DOC) = 0.69 \cdot \ln(EC) - 0.09 \cdot \ln(Ord) - 2.03$	0.34	10,090
Copper	$\ln(Cu) = 1.02 \cdot \ln(EC) - 1.16$	0.04	10,736	$\ln(Cu) = 0.984 \cdot \ln(EC) + 0.015 \cdot \ln(Ord) - 1.07$	0.04	10,738

As a final evaluation of the relative accuracy of each method, DEQ compared the fit between BLM IWQC based on all measured parameters with BLM IWQC based on estimates of all geochemical ions and alkalinity using both estimation methods (**Figure 25**, note the top plot is identical to **Figure 22** and is reproduced here for reference). We found that although the regression on specific conductance + stream order appeared to be slightly more accurate at predicting certain geochemical ion parameters, the root mean square error between observed and predicted values (RMSE) was about 4% lower for the IWQC estimated using specific conductance + stream order, 0.55 µg/L vs. 0.53 µg/L, respectively.

Figure 25: Predicted versus observed values for regression on specific conductance (top) and specific conductance + stream order (bottom).



Therefore, given the very small differences in estimates of IWQC and the RMSE between the two methods, and the negligible improvements in R^2 values for regression equations, DEQ would expect to continue to use specific conductance as a single covariate, rather than using stream order as an additional covariate to estimate geochemical ions.

VI.B Geographically Based Parameter Estimates

In addition to using the specific conductance regression approach, DEQ also evaluated the second EPA method of developing default values for BLM input parameters based on geographical similarities in water chemistry. Water quality parameters, especially the geochemical ions, can co-vary with regional geology and biogeochemical characteristics. DEQ focused on identifying spatial trends in the geochemical ions and alkalinity by using specific conductance data. These parameters are likely to be estimated from specific conductance, and due to low sensitivity to the individual parameters, estimates can be used without degrading the accuracy of the BLM output. Geochemical ions are also most likely to be missing from complete sets of parameters. Because of the sensitivity of DOC and pH in the BLM, DEQ directly examined spatial trends in these parameters.

DEQ evaluated the distribution of sites using several geographic systems to group sites that may share similar water chemistry across the state of Oregon. EPA's Missing Parameter document[60] utilized sample medians for each BLM parameter from sites located within EPA Level III Ecoregions across the United States. Ecoregions define areas of similar landform, soil and plant communities that encompass variation in underlying geology, precipitation and climate—all environmental factors that can influence patterns of water chemistry. There are nine EPA Level-III Ecoregions within Oregon (**Figure 26**). Most of these Ecoregions also extend into adjacent states.

We began by focusing on the distribution of specific conductance data within different regions of the state, because of the high correlation with all the geochemical ions and alkalinity in our database. Relying on this correlation avoided a complicated process of determining relationships for each of the ten individual geochemical ions among all nine of the ecoregions. Additionally, it is highly likely that suitable BLM samples will be missing data for one or more of the geochemical ions and alkalinity. Therefore, we looked at identifying differences in specific conductance as a method to rapidly identify and integrate differences in water chemistry among sites.

Figure 26 shows box plots of the distribution of specific conductance for sites within each Ecoregion. Letters at the top of each box plot indicate regions where the median is not statistically different among regions according to a Kruskal-Wallis one-way analysis of variance, and extends the Mann-Whitney U test of medians to more than two groups. This is a robust nonparametric test of whether two samples come from the same population. For instance, box plots in **Figure 27** and **Figure 29** that have the same letter above them have statistically similar medians and come from statistically similar populations. The results of the Kruskal-Wallis test show that many regions have similar median values of specific conductance among most EPA Level-III Ecoregions (**Figure 27**). There were 36 possible pair wise comparisons for the nine Ecoregions. Six of the pair wise comparisons had no significant difference in the distribution of specific conductance data; identified as sharing the same group letter at the top of the figure. However, the pattern was such that adjacent Ecoregions were similar to the one or two regions adjacent. Only two regions had a median that was statistically different from all other regions. Only sites in the Cascades and the Snake River Plain had median specific conductance that was statistically different from every other region. The similar median values observed among multiple regions suggest either: 1) that there are either no differences in specific conductance data, or 2) distinct differences in geochemical ions and alkalinity among sites are not being captured at the scale of the Ecoregion.

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[60] EPA (2012). Development of Tools to Estimate Water Quality Parameters for the Biotic Ligand Model. Office of Water. April 2012. **820R12008.**

Figure 26: Distribution of BLM sites across EPA Level III Ecoregions

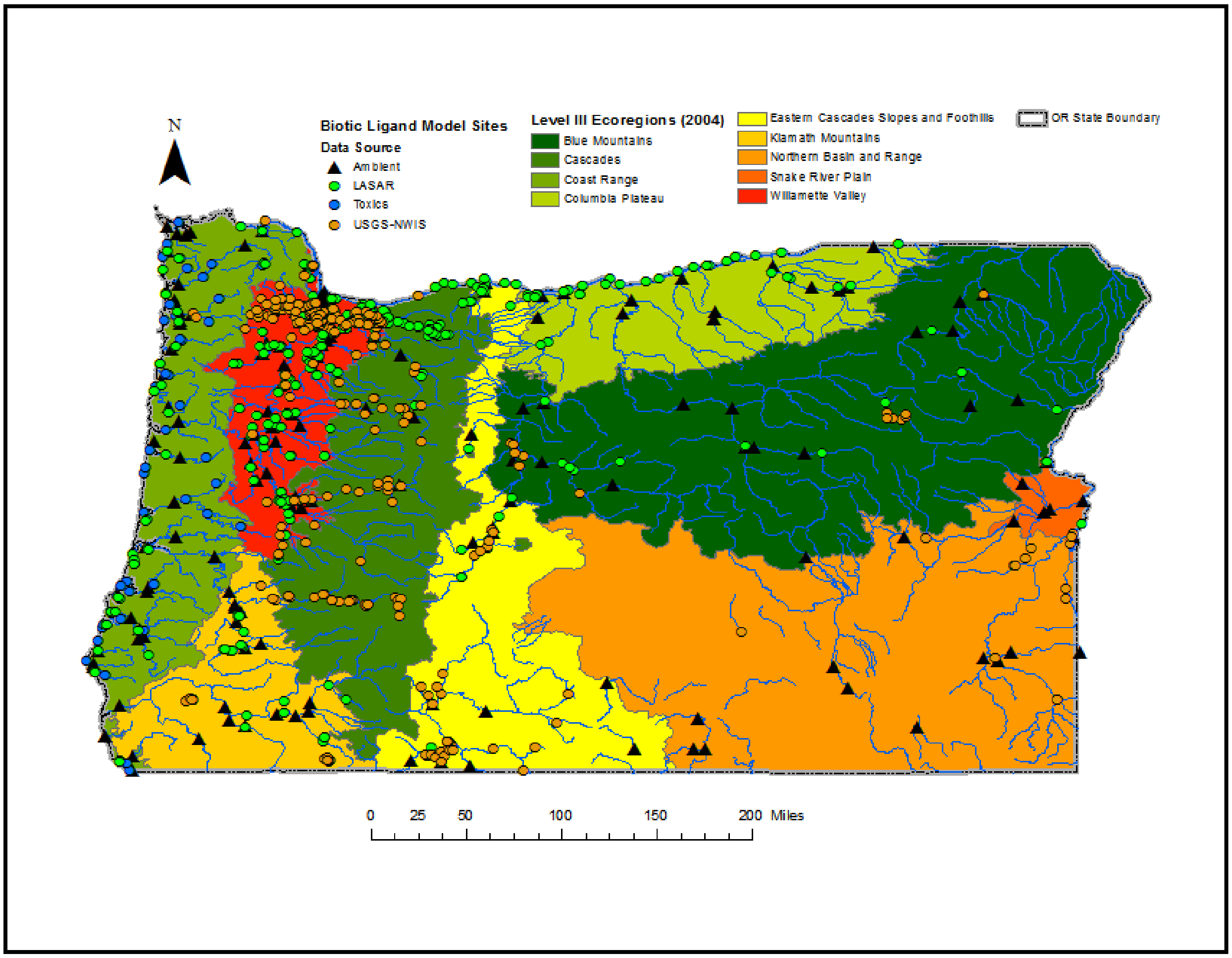
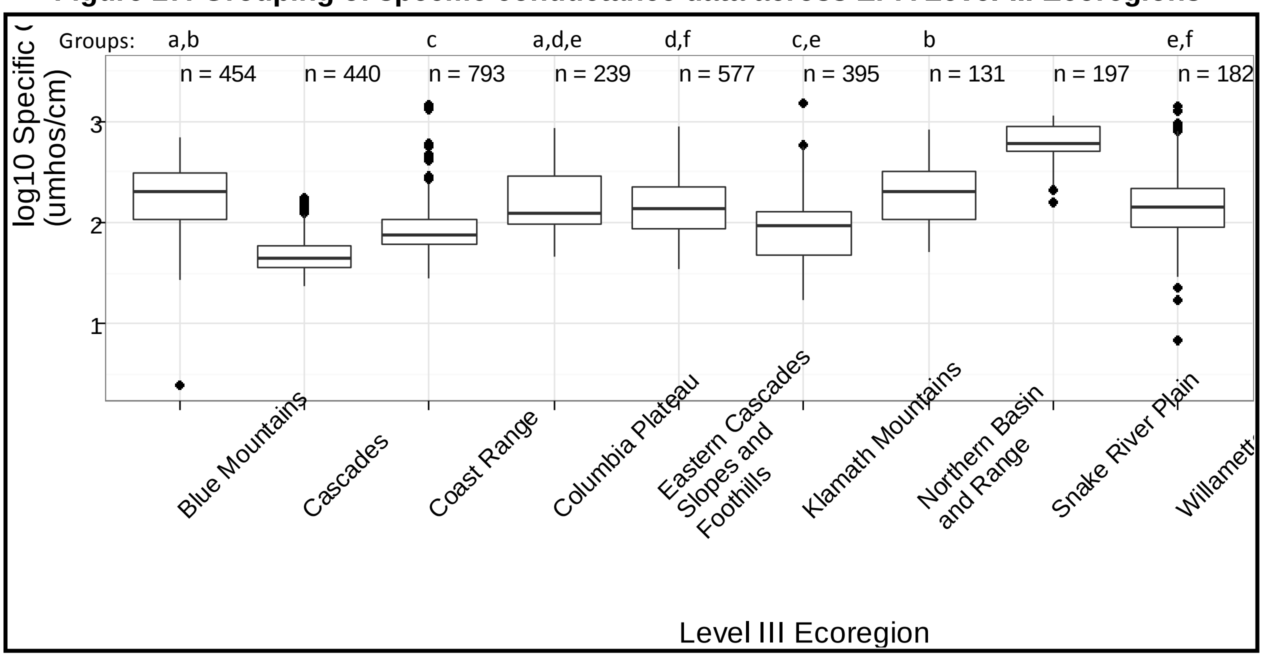


Figure 27: Grouping of specific conductance data across EPA Level-III Ecoregions



DEQ repeated this analysis using the 10 HUC-4 sub-basins as another way to group BLM sites that may have similar water chemistry (**Figure 28**). The Hydrological Unit Code (HUC) is a 6-level classification system used by the U.S. Geological Survey that delineates major drainage areas and nested hydrologic subdivisions within them[61]. The 4th level HUC, also referred to as sub-basins are drainage basins averaging 16,800 square miles. DEQ used the HUC-4 sub-basins because they were the hydrologic units that most closely matched the size of Level-III Ecoregions, which do not necessarily follow hydrologic boundaries.

Similar to the EPA Level III Ecoregion analysis above, DEQ found that the HUC-4 watersheds had very high degrees of overlap in the distribution of specific conductance. There were 10 HUC-4 regions and 45 possible pair wise comparisons, 11 pairs of which were not statistically different. There was a similar pattern to the EPA Level III Ecoregions in that adjacent Ecoregions tended to have statistically similar medians, and no HUC-4 distribution was significantly different from all other HUC-4 distributions (**Figure 29**). However, the accuracy of the distribution for the Sacramento sub-basin is questionable due to a very low sample size (n=11).

[61]USGS. Hydrologic Unit Maps. http://water.usgs.gov/GIS/huc.html. U.S. Geological Survey. Accessed Jan. 6, 2016.

Figure 28: Distribution of BLM sites across HUC-4 sub-regions

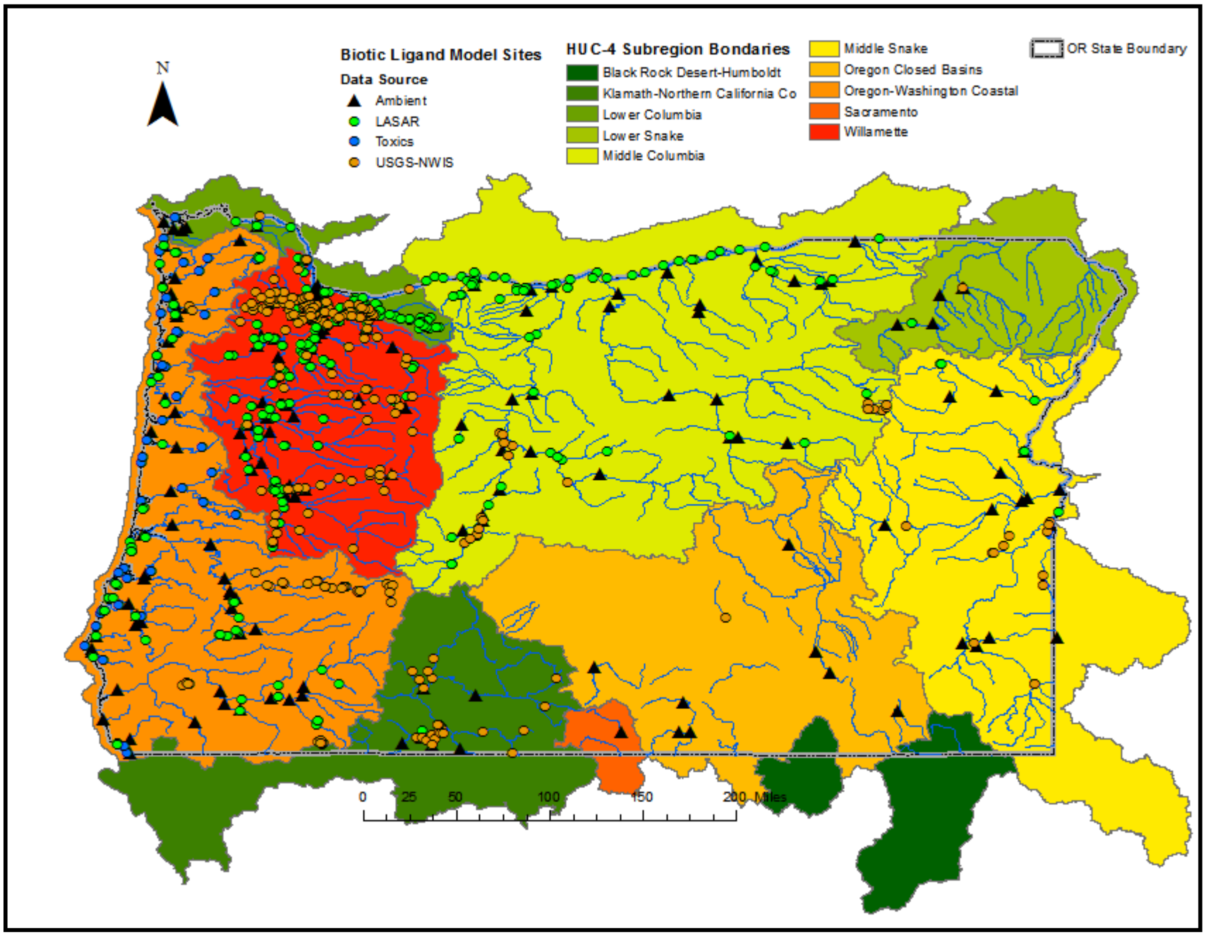
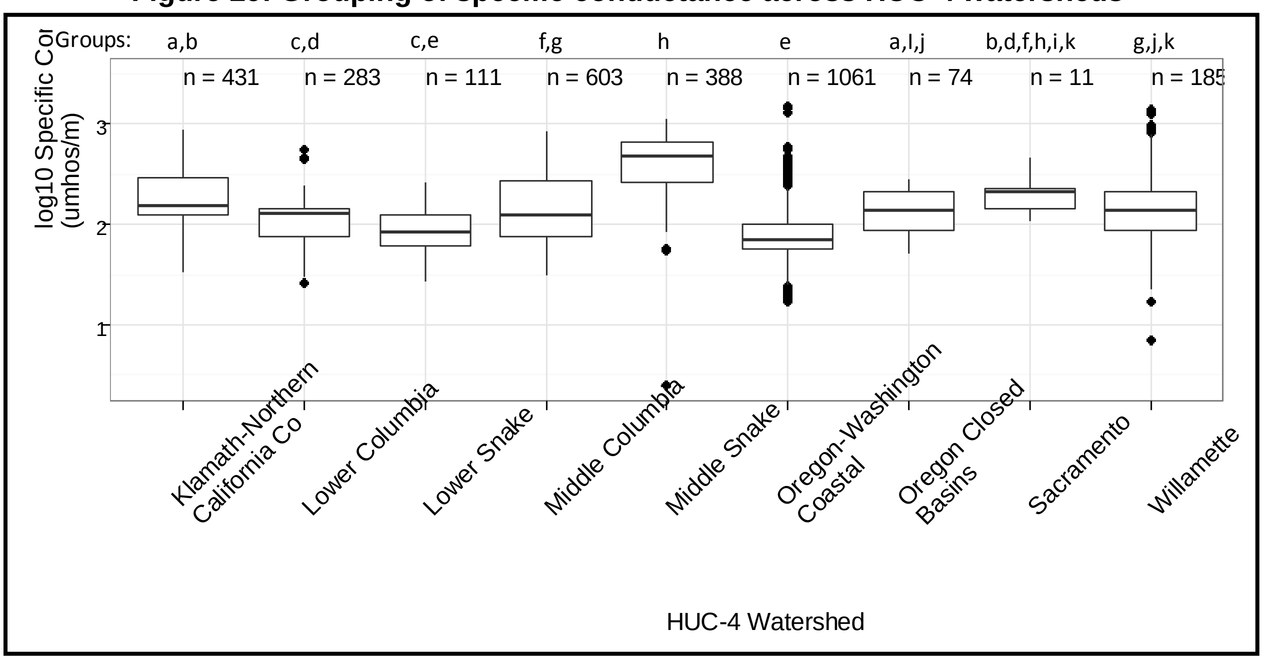


Figure 29: Grouping of specific conductance across HUC-4 watersheds



In order to confirm that we are capturing an underlying pattern in water chemistry that differs among regions, we would expect some statistic, such as a median or some percentile, to demonstrate a statistical difference from region to region. We did not find a strong statistical difference in the median of specific conductance data among the nine Level-III Ecoregions or ten HUC-4 watersheds. The 10th percentile of the specific conductance data was also comparable among Level III Ecoregions, except for the Snake River Plain and Columbia Plateau, which deviated by more than 10%. Although in the Level-III Ecoregions analysis, there were distinct differences in median and 10th percentile specific conductance data between the Cascade and Snake River Plain Ecoregions from the other Ecoregions. While ample conductivity data were available, the number of sites with complete measured parameters in these Ecoregions was very small: n=4 for Cascades and n=1 for Snake River Plain.

There were not many geographic units with significant differences in the distributions of DOC and pH data from all of the other geographical units for EPA Level-III Ecoregions or HUC-4 watersheds (**Table 23**). DEQ also analyzed the distribution of specific conductance, DOC and pH for HUC-6 basins, which average 10,500 square miles. Due to reduced sample size within basins due to the finer scale of these hydrological units, there was not a large enough sample size to make accurate comparisons.

Table 23: Median, 10th percentile, and grouping of similar ANOVA results for means of DOC and pH in Level-III Ecoregions and HUC-4 sub-basins

	DOC			pH		
Level-III Ecoregion	**10th %**	**Median**	**Group**	**10th %**	**Median**	**Group**
Blue Mountains	1.1	2.6	a	7.89	8.3	a
Cascades	0.083	0.83		7.1	7.3	
Coast Range	0.83	1.3		6.9	7.5	
Columbia Plateau	1.3	2.4	a,b	7.82	8.2	a,b
Eastern Cascades Slopes and Foothills	0.83	5.85	a,c	7.5	7.9	a,c
Klamath Mountains	0.83	1.7		7.7	8	
Northern Basin and Range	0.937	2.95	a,b,d	7.86	7.9	a,c,d
Snake River Plain	2.41	3.5		8.5	8.5	a,b,d
Willamette Valley	0.83	2.3	b,c,d	7.1	7.6	
HUC-4 Subregion	**DOC**			**pH**		
	10th %	**Median**	**group**	**10th %**	**Median**	**group**
Klamath-Northern California	1.78	3.7		7.84	8	a
Lower Columbia	1.4	1.8	a	7.2	7.8	b
Lower Snake	1.85	2.75	a,b	7.7	8.05	a,c
Middle Columbia	1	2.3	b,c,d	7.64	8.2	c
Middle Snake	2.32	2.7	d	7.98	8.2	a,c,d
Oregon-Washington Coastal	1	1.8		6.9	7.4	
Oregon Closed Basins	1.95	4.45	b,c,d,e	7.83	7.9	a,c,d
Willamette	0.67	1.6	b,d,e	7.1	7.4	b

DEQ initially focused the evaluations on the distribution of specific conductance within regions because it was a strong correlate with all the geochemical ion parameters. Since the Level-III Ecoregions had more statistically significant differences in specific conductance distribution among regions, we further investigated the pattern of similarity in an attempt to define regions for the purpose of BLM assessment that might capture geographic variability in the water chemistry of the BLM parameters. Ecoregions that shared a group letter also tended to be adjacent to one another (**Figure 26**). DEQ combined adjacent Level-III Ecoregions sharing a group letter to propose distinct physiographic regions that capture a slightly coarser scale of landscape variability in Oregon. We identified four new physiographic regions by merging Level-III Ecoregions based on similarities in specific conductance data. These are Coastal, Willamette Valley, Cascade and Eastern physiographic regions (**Figure 30**). Data sample coverage in these regions is described in **Table 24** and **Table 25**. As proof of this coarser grouping, DEQ found that the distribution of specific conductance data within these four physiographic regions were all statistically different according to the Kruskal-Wallis test (**Figure 31**). The notches in the box plots represent a 95% confidence interval of the median. In addition to specific conductance, DEQ found that the distribution of DOC data was also statistically different among these new physiographic regions **(Figure 32**). We also found that pH fell into two groups, with a similar distribution between the Coastal and Cascade physiographic region, and the Willamette Valley and Eastern physiographic regions (**Figure 33**). Therefore, DEQ defined four new physiographic regions that can simplify BLM evaluations over either of the nine Level III Ecoregions or the 10 HUC 4 watersheds.

Table 24: Sampling sites in the proposed physiographic regions

Region	**Sites (n)**
Coastal	175
Willamette Valley	329
Cascades	105
Eastern	203
Total Sites	**812**

Table 25: Number of complete sets of BLM samples per proposed region and per season

By Region	Sample size
Coastal	201
Willamette Valley	71
Cascades	41
Eastern	48
Total	**361**
By Season	**Sample size**
Wet	220
Dry	141
Total	**361**

Figure 30: Distribution of BLM sites across proposed physiographic regions

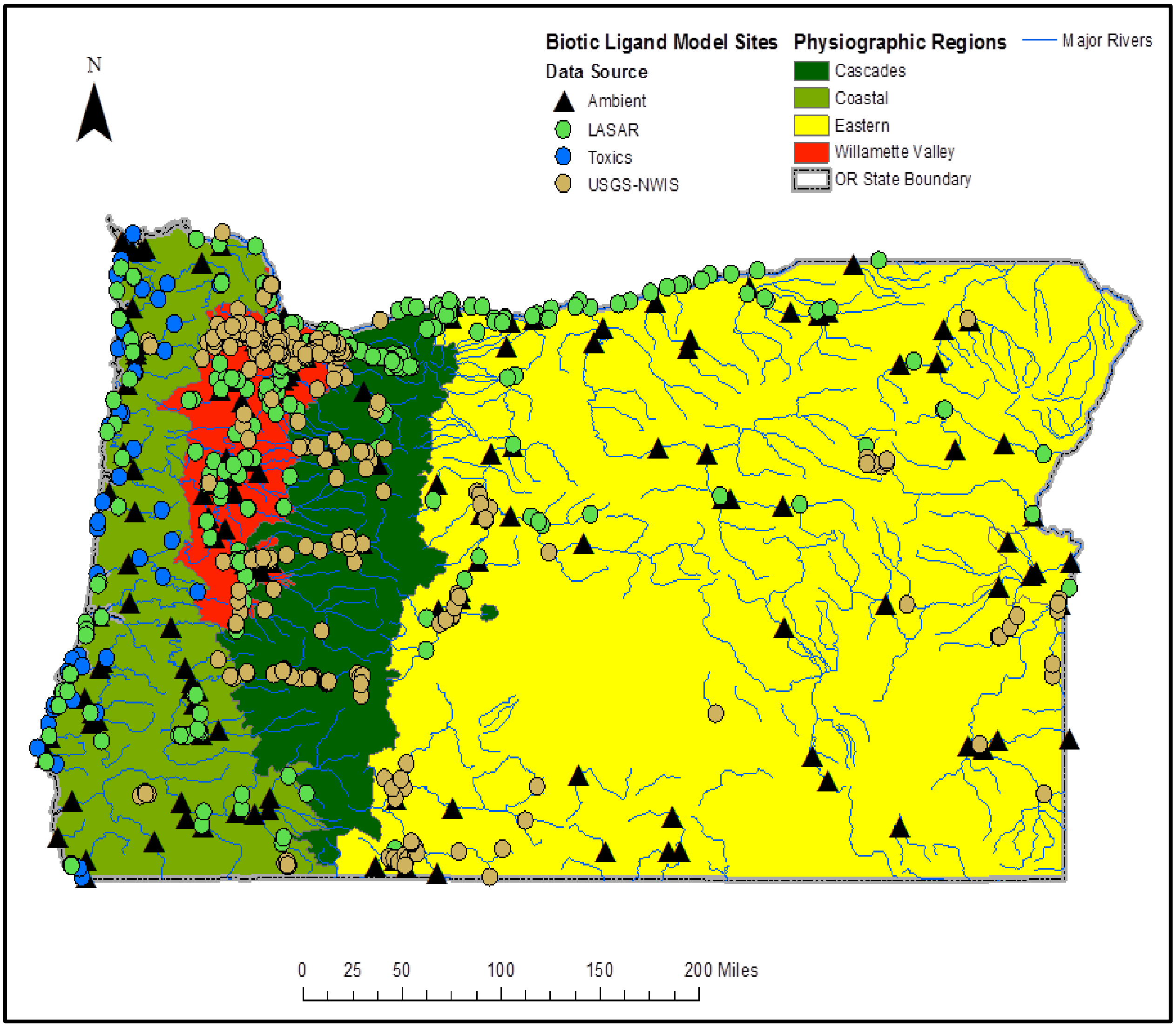


Figure 31: Grouping of specific conductance across proposed BLM physiographic regions

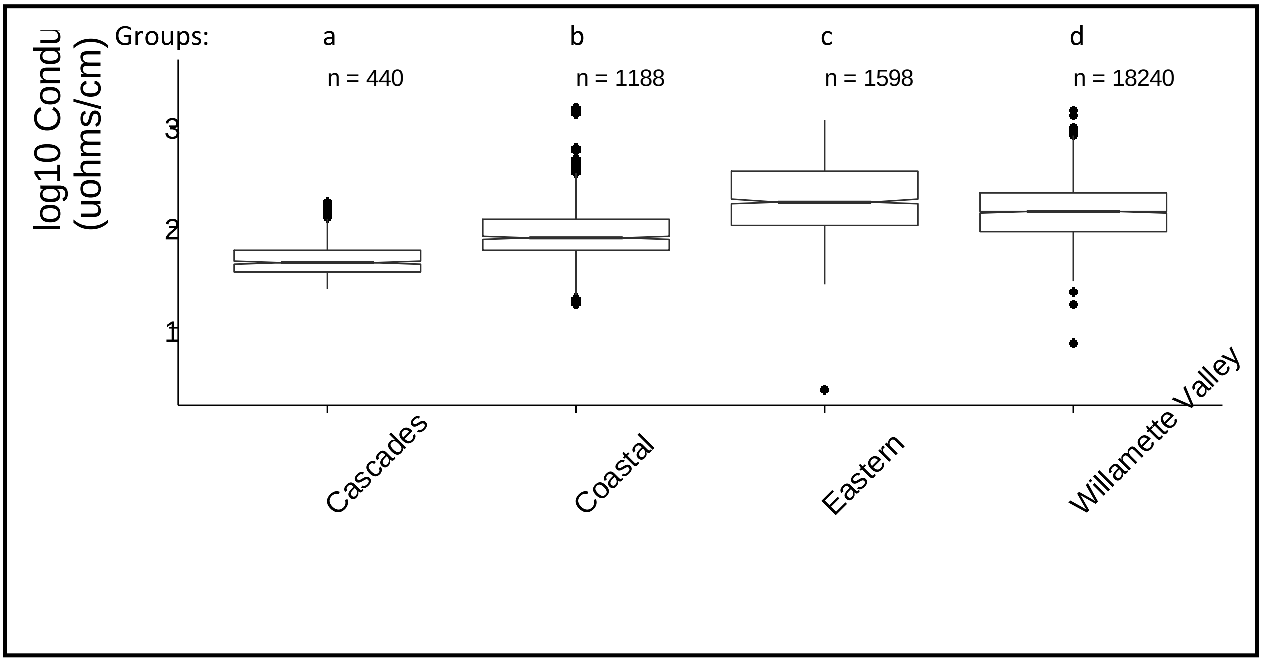


Figure 32: Grouping of DOC across proposed BLM physiographic region

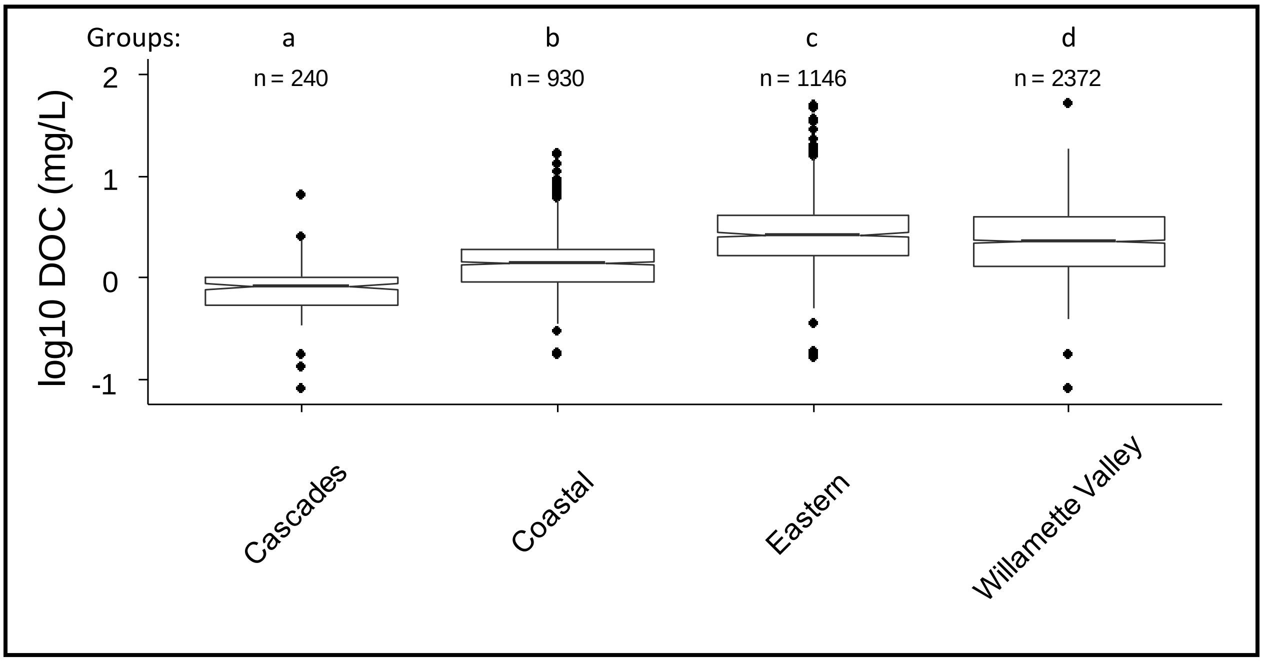
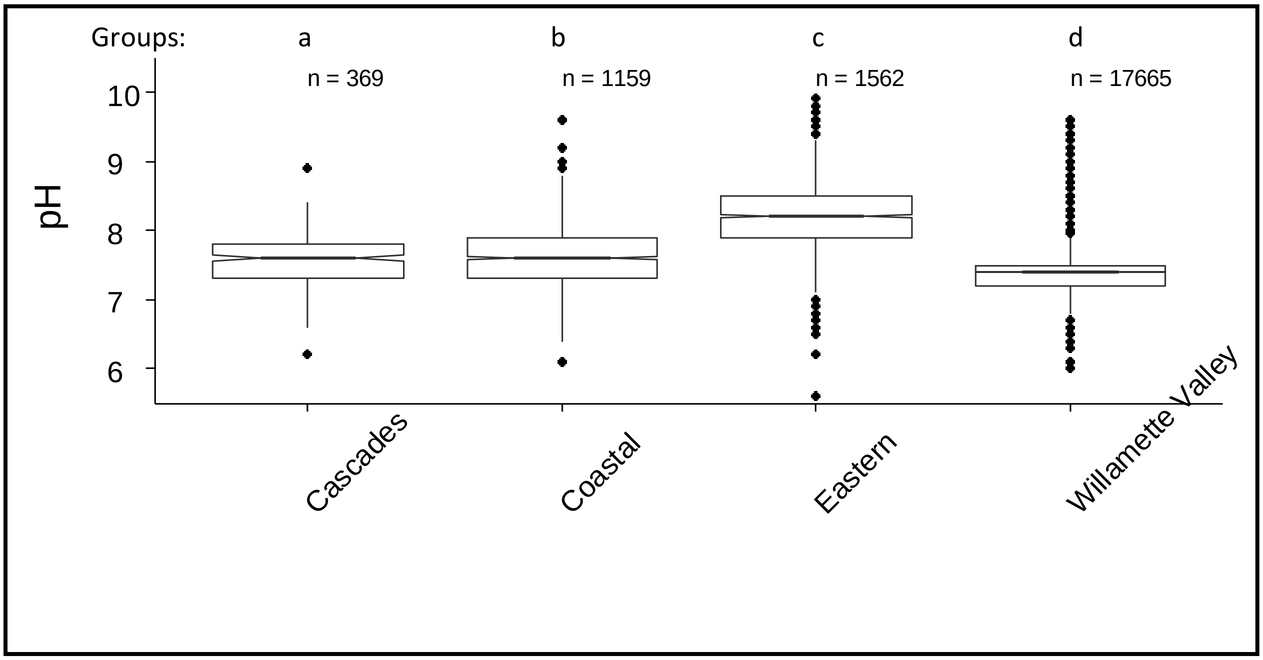


Figure 33: Grouping of pH across proposed BLM physiographic regions



The grouping of sites into physiographic regions with distinct distributions of BLM parameters based on differences in specific conductance, DOC and pH is a potential simplifying method for assigning values to missing parameters. Sites with missing values for BLM input parameters could be assigned the median, geometric mean or some percentile of those parameters based on a physiographic region.

DEQ evaluated the effect of substituting physiographic regional median values of all BLM parameters except pH and temperature for missing parameters on IWQC results following the same procedures used to evaluate the specific conductance-based method described in section VI.A.1. Starting with the Complete Measured Database **(Table 16, Appendix A**), DEQ substituted the median value for each parameter from the proposed BLM physiographic region where samples were located.

The result of stepwise substitution of parameters with physiographic regional medians is shown in **Figure 34**. The y-axis shows the estimated BLM IWQC based on the median physiographic region value for the parameter shown in each panel, while the other parameters use measured values. The x-axis shows the actual IWQC based on all measured parameters. The dashed line is a 1:1 line showing when the estimated IWQC and measured IWQC are equal. There was poor agreement between IWQC based on measured parameters versus IWQC based on physiographic median DOC. There was good agreement between measured and estimated IWQC for substitutions of the physiographic regional median for each geochemical ion.

Figure 34: Comparing measured to estimated IWQC using physiographic regional median values, by parameter

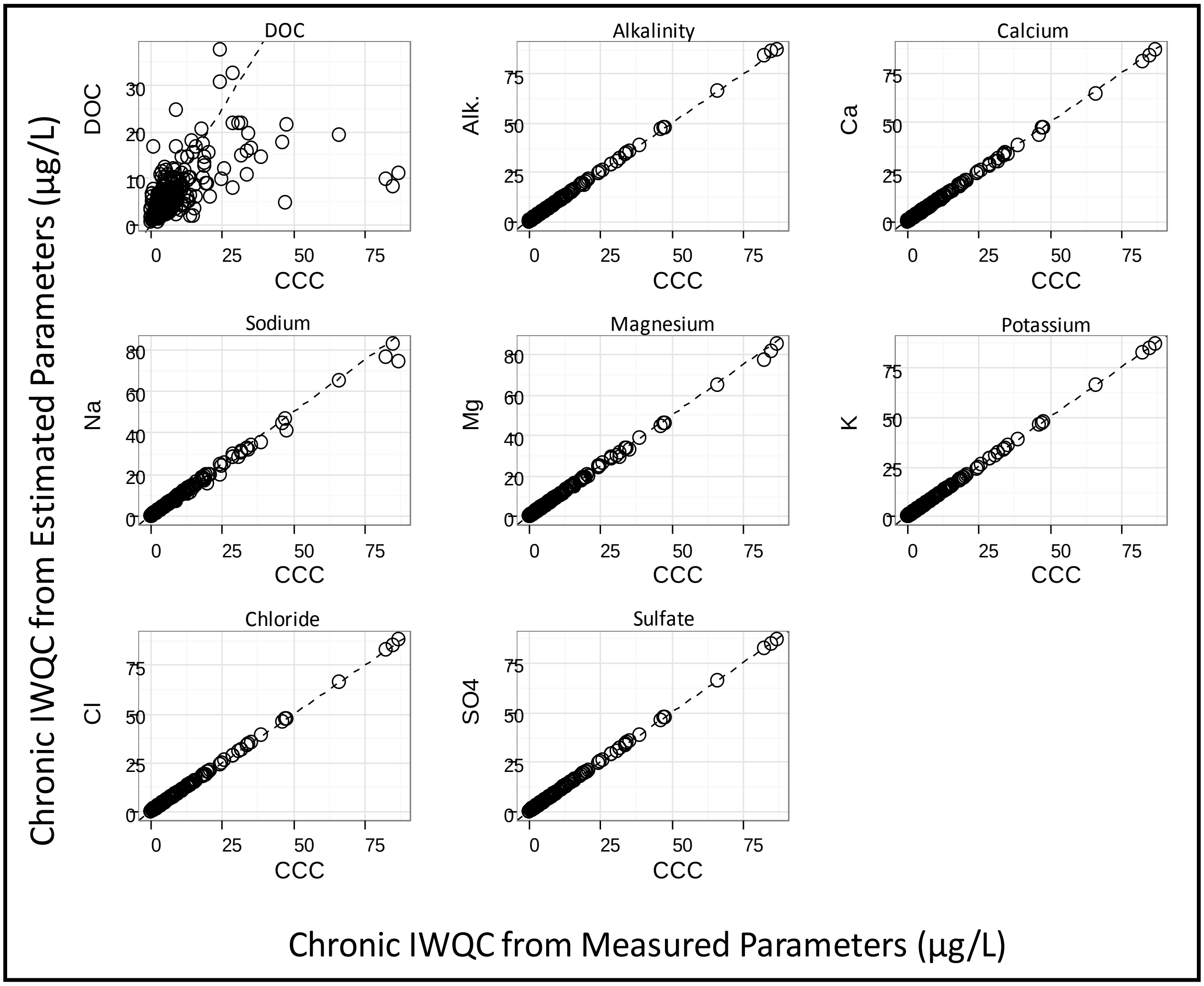
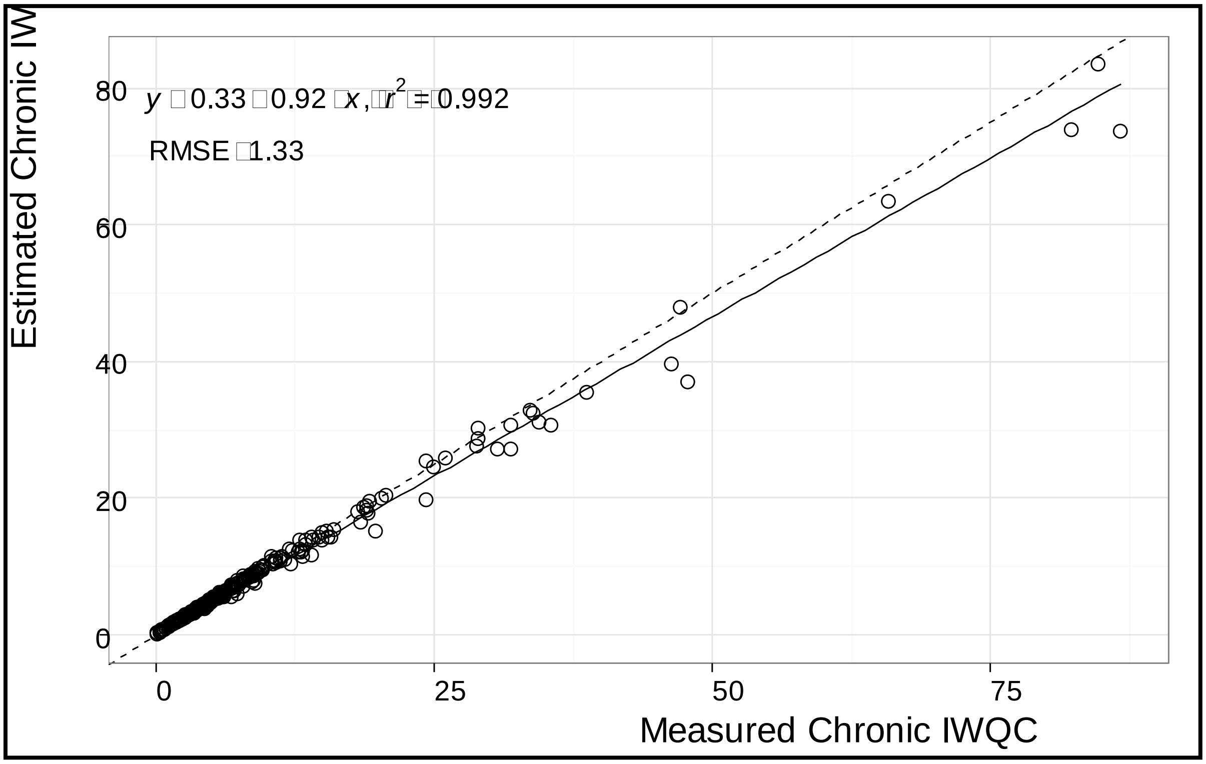


Figure 35: Comparing measured to estimated IWQC using regional median values (except DOC, pH and temperature)



DEQ then derived BLM IWQC by substituting all values with regional medians except for DOC, pH and temperature. The results of this analysis are in **Figure 35**. The y-axis shows the IWQC using regional medians, and the x-axis shows the IWQC using measured values of all parameters. The dashed line is the 1:1 line where measured and estimated IWQC are equal. The solid line is an OLS regression passing through the origin, with a slope of 0.93. The results of the regression and the root mean square error of the estimates are at upper left. There was relatively good agreement between estimated IWQC and measured IWQC, with an adjusted R^2 of 0.992 and a RMSE of 1.33 µg/L. These errors are slightly lower than the typical analytical detection limit of 1.5 µg/L copper in our database. There also appeared to be a slight negative bias in the estimated IWQC. The accuracy of calculated IWQC had a better fit (R^2 >0.999), and lower error (RMSE 0.55 µg/L) when using the conductivity regression approach to estimate missing geochemical ion data than using regional medians of observed ion concentrations (see section VI.B).

DEQ's sensitivity analysis in section V.C.1 and our evaluation of using estimated parameter values to calculate IWQC in this section show that estimating geochemical ion concentration through regression using specific conductance is robust and unlikely to have significant impacts on BLM outcomes when missing data needs to be estimated. However, achieving accurate measurements or estimates of DOC and pH remains critical. The substitution of estimated values for these sensitive BLM parameters resulted in poor agreement between IWQC calculated from measured and estimated data.

VI.C Assessment of Potential Regional BLM Criteria

The factors on which BLM sites can be grouped for evaluation of potential BLM criteria according to similar water chemistry are:

- Specific conductance; as a positive covariate to the geochemical ions and alkalinity;
- DOC; and
- pH

In section VI.C, DEQ derived physiographic regions based on an aggregated map of EPA Level III Ecoregions that contained similar parameter distributions. This resulted in regions with distinct distributions of the most important BLM input parameters. Presumably, sites with similar water chemistry are likely to have similar IWQC values under the BLM framework. These regions provide a potential framework for developing regional BLM criteria by aggregating IWQC calculated from multiple sites within each physiographic region (**Figure 36**).

The distribution of IWQC in these proposed regions, calculated from a set of samples from the Complete Measured Database (Appendix A), is shown in **Figure 37**. The distribution of IWQC for the Cascades and Eastern region were statistically different, as determined by a Kruskal-Wallis test. The distribution of IWQC for the Willamette Valley and the Coastal region were different from the other regions, but not statistically different from each other. The IWQC values for these two regions show a much higher range for outliers than the Cascade and Eastern regions, although variability, but not range, in the Eastern region also appeared high.

Figure 36: Proposed BLM assessment regions for Oregon

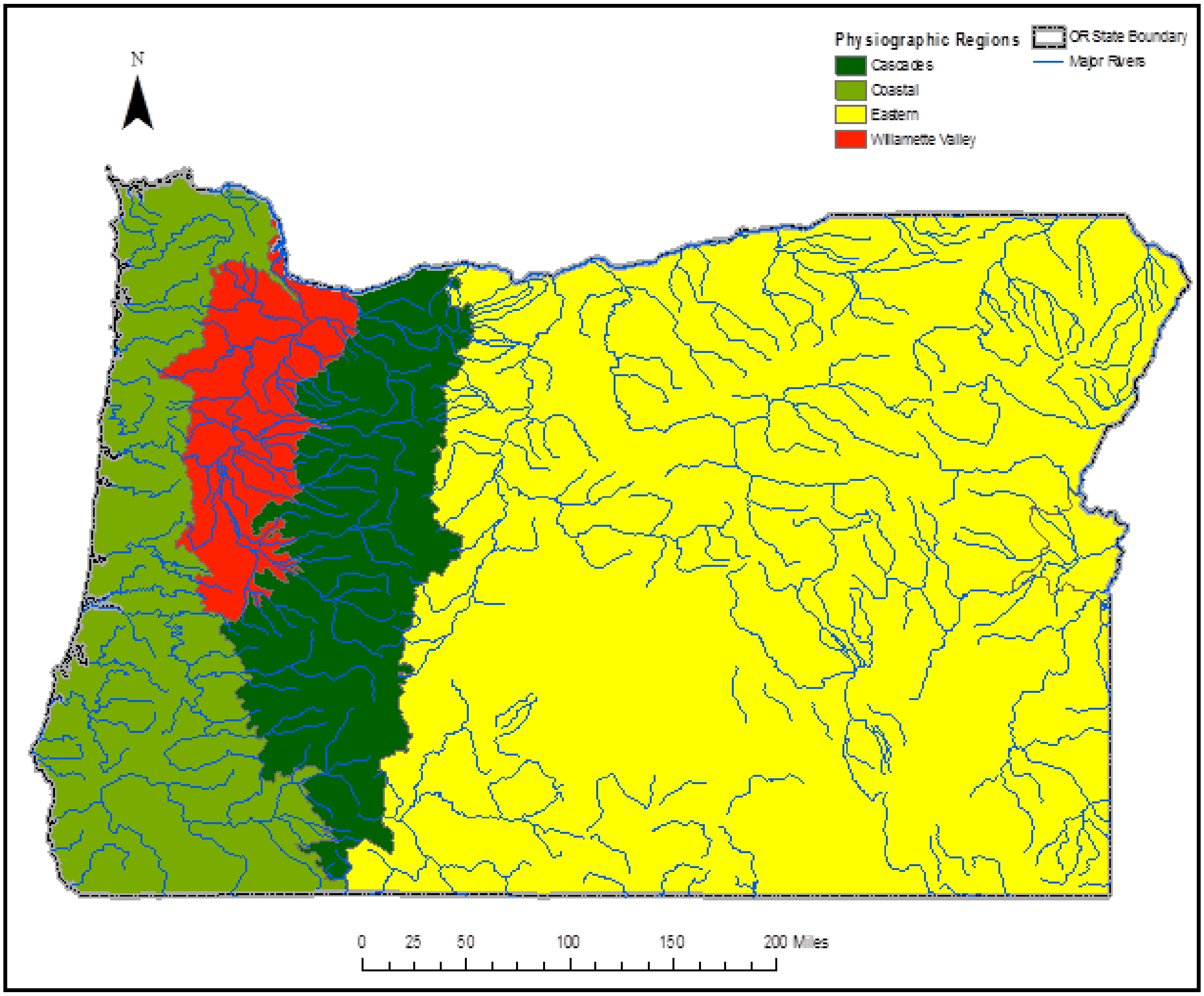
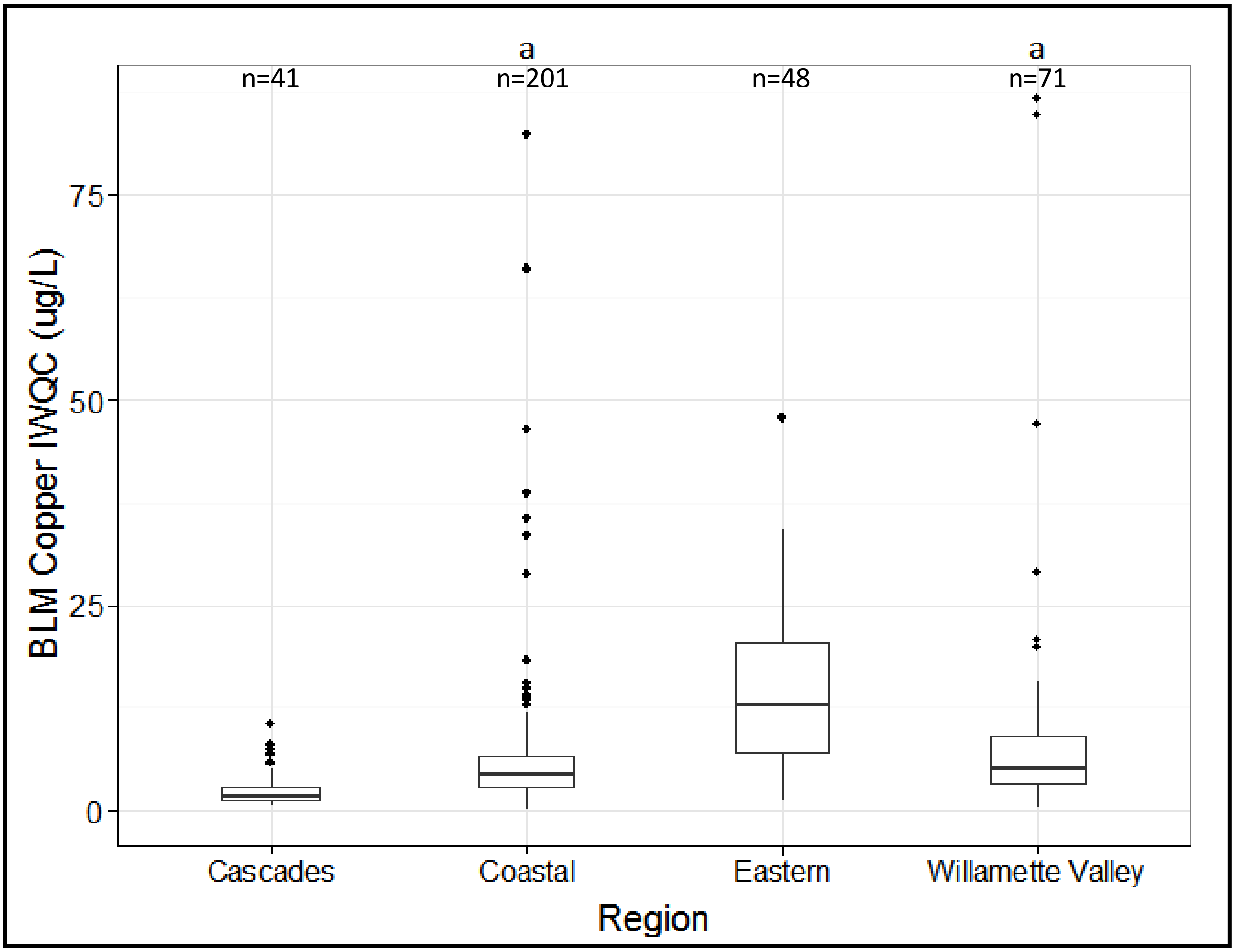


Figure 37: Statistical distribution of copper IWQC in the physiographic assessment regions



VI.D Results Summary

- DEQ must rely on a combination of available data and estimates for some parameters to apply the BLM until additional data is collected.
- In some locations, data for the geochemical ions or for organic carbon is available as a total concentration, but not as a dissolved fraction concentration. Future data collection for BLM purposes should measure dissolved concentration of parameters.
- DEQ's analysis shows that there is a strong basis for using total concentration data for geochemical ion and alkalinity parameters to apply the copper BLM where dissolved concentration data are not available. However, use of total concentration data should be subject to best professional judgment and compared to BLM calibration ranges for the parameter in question.
- Where only TOC data are available, DOC may be estimated from TOC. Our analysis suggests selection of a conversion factor between 0.83 and up to 1.0, may be appropriate to convert from TOC to DOC data from the Willamette and Eastern Oregon. However, there is high uncertainty in

the accuracy of these coefficients for the Coastal and Cascade regions due to small sample size and high variability in the data.

- DEQ may cautiously use total recoverable Cu results when dissolved Cu results are greater than total recoverable Cu results, indicating potential sample contamination or some other data quality issue, or when dissolved Cu results are not available, or would be expected to vary in receiving water depending in part on the amount of suspended solids present.
- DEQ found strong correlations in the Oregon dataset between geochemical ion and alkalinity values with specific conductance. DEQ also analyzed the relationship between IWQC calculated using only measured BLM input values and IWQC calculated using geochemical ions and alkalinity estimates based on specific conductance data. The R^2 between measured and estimated IWQC was >0.99 for both parameters. Therefore, DEQ concludes that using statewide regression equations based on specific conductance is a reasonably accurate method to estimate geochemical ion and alkalinity values for purposes of deriving BLM criteria for copper.
- Given the poor correlation of DOC and pH with specific conductance and the high sensitivity of BLM outputs to these parameters, specific conductance is not suitable to estimate DOC or pH values. In order to calculate accurate IWQC, the BLM should use measured values of DOC and pH parameters. Where measured values are not available, it may be necessary to use a conservative estimate based on the best available measured data.
- Using stream order as an additional covariate to specific conductance slightly improved the prediction of individual geochemical ions, but did not improve accuracy of DOC or pH values. Therefore, DEQ will use conductivity as a single covariate, rather than adding stream order as a covariate, to estimate geochemical ion values.
- The root mean square error of IWQC calculated from median concentrations of geochemical ions across the four physiographic regions was nearly twice that of IWQC calculated using conductivity regressions.
- Best practices would be to use measured temperature and pH data, as DEQ could identify no reasonable method for estimating these parameters.
- On a case-by-case basis, users may be able to estimate temperature using regional or upstream temperature data from nearby monitoring sites. While DOC and pH had statistically similar sample medians and therefore fell into the same four physiographic groups as the other parameters, DOC and pH should not be immediately estimated on this basis given BLM sensitivity to these parameters.
- Physiographic regions that have distinct distributions of water quality parameters may form a rational basis for deriving conservative estimates of copper criteria for sites where certain BLM data are not available.
- BLM copper IWQC for the four different physiographic regions, calculated using only measured data, are from different distributions according to a Kruskal-Wallis test performed on log-transformed IWQC. The Coastal and Willamette Valley regions did not have statistically different IWQC. This may be due to higher variability in IWQC values within these regions.

VII. Using BLM Estimates to Derive Criteria

The majority of samples in the BLM database do not have complete sets of measured parameters (see **Table 16**). DOC is an especially limiting parameter, and it is likely that there are currently insufficient data to calculate IWQC values for many locations in the state that have partial data sets for other BLM parameters. Although the less sensitive geochemical ions can be reliably estimated using empirical regression relationships between these parameters and specific conductance, this method is not suitable to estimate DOC, pH and temperature data. However, it is likely that DEQ will need a method to provide reasonable estimates of these parameters.

The following sections describe two potential approaches for utilizing the BLM to provide conservative estimates for copper criteria in areas or locations where there are not sufficient DOC, pH and temperature data to generate IWQC. The first approach relies on filling BLM data gaps for a specific location by estimating missing parameters using a summary of data from all sites within the same physiographic region. The second approach relies on calculating the IWQC where measured DOC, pH, temperature and specific conductance data are available and selecting a conservative level of the IWQC to employ as a default screening level criterion at sites for locations in the region that lack sufficient BLM data.

VII.A Evaluation of Using Estimated DOC

EPA developed DOC estimates to derive conservative BLM criteria for sites where measured DOC data are not available. EPA's Missing Parameters document[62] provides estimates of DOC concentration for Level III Ecoregions (**Table 26**) based on a combination of a kriged geospatial dataset of nationwide DOC concentrations from two sources: 1) the National Organic Carbon Database (NOCD), compiled with data from USGS –NWIS and EPA–STORET, and 2) the EPA's National Wadeable Streams Assessment (WSA). The USGS sampling is concentrated in un-impacted research streams, and the WSA is limited to samples collected in streams shallow enough to wade, around Stahler stream orders of 1-5. EPA selected sites from each database using a probability-based random sampling design of sites from these two databases in order to reflect the full range in character and variation in streams. The EPA document provides three estimates: the 10th percentile and median of DOC concentration from kriged estimates, and a recommended 10th percentile DOC concentration, which is the lowest 10th percentile of DOC from either the kriged data or the WSA (**Table 26**).

EPA's Missing Parameters document utilized data to provide a randomly selected, representative sample of background water chemistry in surface waters of the U.S. Therefore, this document strongly represents un-impacted water bodies and headwater streams. In contrast, the DEQ database represents the broad range of potential water quality parameters that would be encountered in the state given the range of

[62] EPA (2012). Development of Tools to Estimate Water Quality Parameters for the Biotic Ligand Model. Office of Water. April 2012. **820R12008.**

monitoring locations in the database. Although it may not be as well suited for extrapolation as the EPA database, it represents the range of parameter values over which the model is to be applied. This includes both un-impacted reference streams and receiving waters, where water chemistry, and the resulting BLM criteria, may reflect the effect of multiple impacts from human uses and disturbance.

The DEQ developed a set of broad physiographic regions based on the EPA Level III Ecoregions using data from the Oregon database, which is a combination of data from the USGS-NWIS and data collected by the DEQ (see **Figure 30**). DEQ created these four physiographic regions by merging adjacent Level III Ecoregion zones to form new boundaries where the distribution of geochemical ion concentrations, DOC and pH showed unique statistical distributions of these parameters. DEQ calculated the 10^{th} percentile and median DOC[63] for both the Level III Ecoregions and the Oregon physiographic regions. For Level III Ecoregions, the DEQ estimates for median and 10^{th} percentile DOC tended to be lower than EPA's median and 10^{th} percentile values for the NOCD data (see **Table 26** to compare the EPA and DEQ values). However, the data from the wadeable streams assessment resulted in the EPA recommended 10^{th} percentile data being lower than the DEQ 10^{th} percentile data for each Ecoregion.

[63] DEQ converted TOC data to DOC data using a translator of 0.83.

Table 26: Level-III Ecoregion estimates of DOC concentration

	EPA			DEQ	
Level-III Ecoregion	**10th %** (EPA 2012, Table 8, NOCD)	**Median** (EPA 2012, Table 9, NOCD)	**Recommended 10th %** (EPA 2012, table 10, NOCD and WSA)	**10th %**	**Median**
Blue Mountains	1.34	3.10	0.804	1.1	2.6
Cascades	0.30	1.40	0.310	0.08	0.83
Coast Range	1.12	2.20	0.659	0.83	1.3
Columbia Plateau	2.04	3.60	0.510	1.3	2.4
Eastern Cascades Slopes and Foothills	1.42	2.30	0.500	0.83	5.85
Klamath Mountains	1.70	2.60	0.554	0.83	1.7
Northern Basin and Range	1.81	3.20	0.954	0.937	2.95
Snake River Plain	2.20	NA	2.200	2.41	3.5
Willamette Valley	1.07	2.90	1.070	0.83	2.3

Table 27: DEQ physiographic region estimates of DOC concentration

	DOC	
DEQ Physiographic Region	**10th %**	**Median**
Cascades	0.083	0.83
Coastal	0.83	1.4
Eastern	1.00	3.1
Willamette Valley	0.83	2.3

DEQ compared the relative effect of each set of DOC estimates (i.e. 10th percentiles and medians from tables 21 and 22) on IWQC values using each set of DOC estimates by using a similar procedure to the evaluation of physiographic region estimates in section VI.C. First, DEQ calculated the IWQC using a Complete Measured Database (**Table 16** and Appendix A). Next, DEQ created new data tables by substituting all measured DOC values with the EPA or DEQ estimates, and re-calculated the resulting IWQC for each set of substitutions.

The DEQ estimate of median DOC was high relative to the EPA estimates for the Eastern Slopes and Cascades Ecoregion (**Table 26**). This resulted in a number of paired observations that were outliers when compared to IWQC estimated using the EPA's median estimate (**Figure 38**). Because these outlier estimates were based on a median from a small number of samples, DEQ omitted these outliers when comparing measured and estimated IWQC values. IWQC calculated for Level-III Ecoregions from DEQ estimates tended to be similar to the IWQC calculated from EPA estimates. In **Figure 39**, the dashed line represents the 1:1 line, while the solid line represents the best fit of an OLS regression. The regression equation, R^2, and root mean square error (RMSE) are shown at the upper left in each panel. The estimates of IWQC using both the 10th percentile and median DOC estimates from the Oregon database also tended to be lower than IWQC calculated from DOC estimates provided by the EPA (**Figure 39**).These results reflect the generally lower summary statistics for DOC concentration in the DEQ database (**Table 26**) compared to EPA DOC concentration. There was better agreement between IWQC estimates using the 10th percentile of DOC (RMSE 1.86 µg/L) than the median DOC (RMSE 3.76 µg/L).

Figure 38: Comparing chronic IWQC estimates in Level-III Ecoregions using data from the Oregon BLM Database and the EPA Missing Parameters Document database.

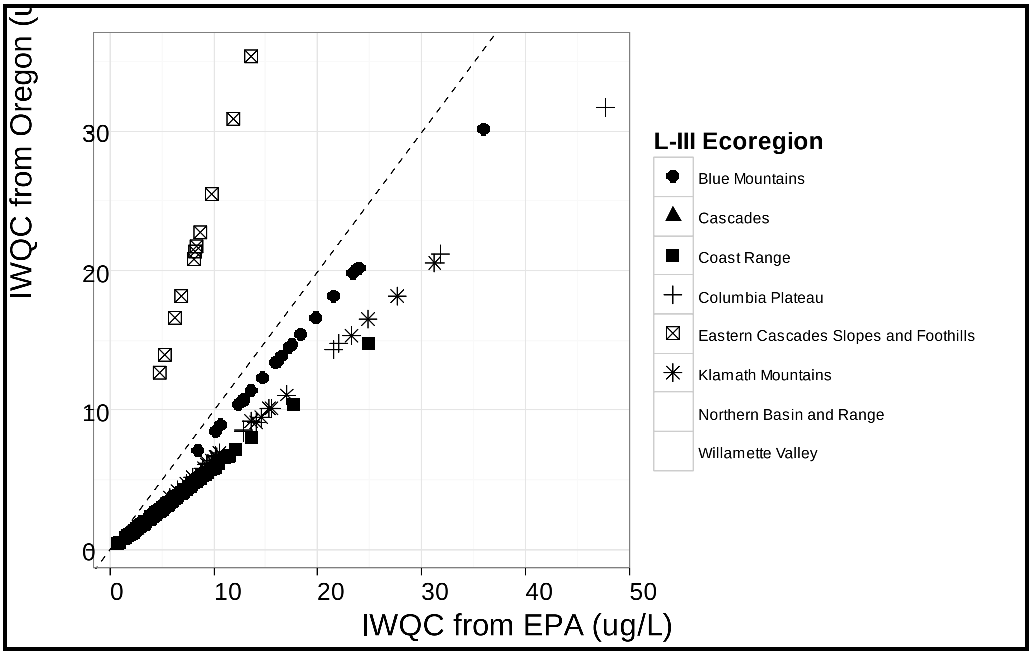
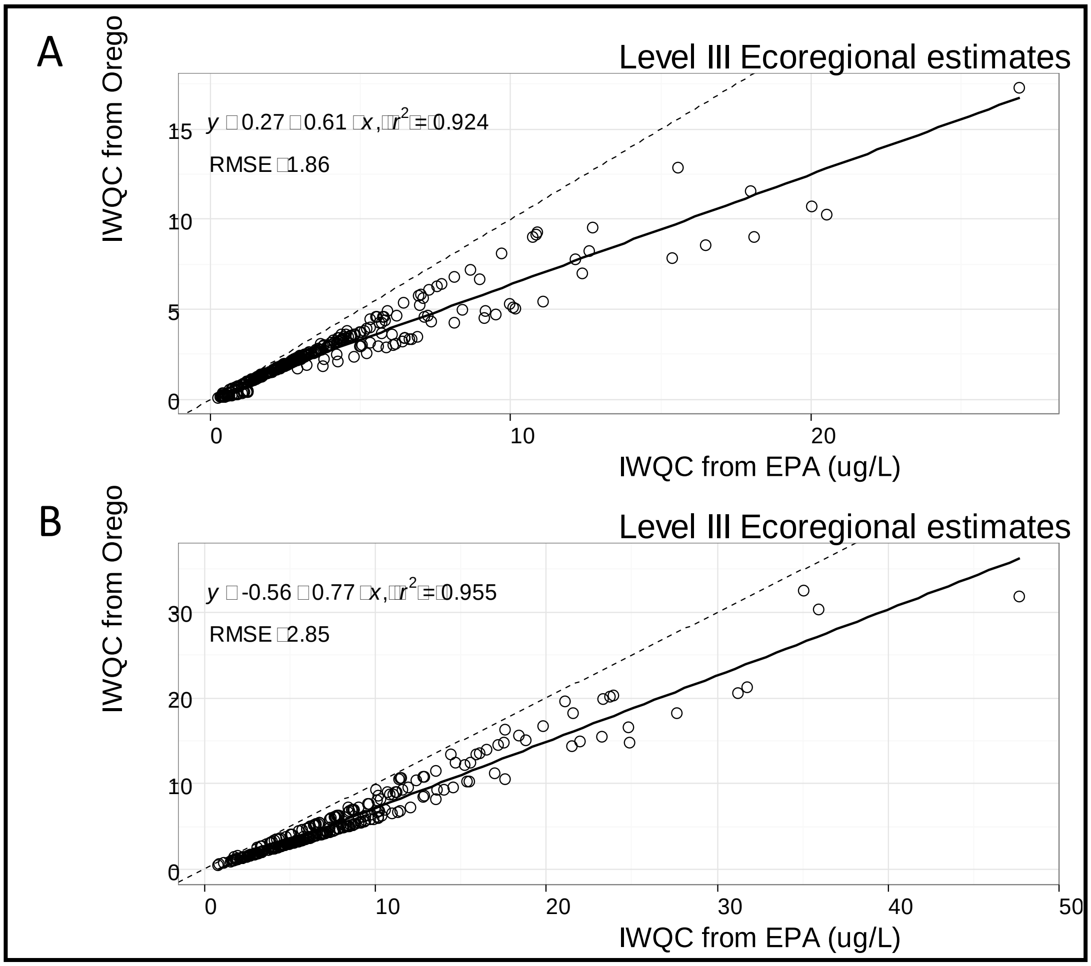


Figure 39: Comparison of chronic IWQC estimates in Level-III Ecoregions using data summarized from the Oregon BLM database and from the EPA Missing Parameters document.



The distribution of IWQC values calculated from estimates of DOC is shown in (**Figure 40**). From left to right: the distribution of IWQC calculated from actual measured data; the median DOC of EPA's NOCD data; the recommended 10th percentile value, representing the lowest 10th percentile value from either the NOCD and WSA databases; the median DOC from the Oregon database; the 10th percentile from the EPA's NOCD database; the 10th percentile from the Oregon database. The median IWQC calculated from estimated DOC data tended to be lower than IWQC values from measured data (**Figure 40**, actual first bar from left). This is an expected result because the median, and in particular, the 10th percentile values are conservative estimates and would therefore tend to bias results to lower IWQC values. The EPA-recommended estimated values of DOC, a combination of the most conservative estimates using either kriged geospatial data or data from the Wadeable Streams Assessment, provided the lowest estimates of median IWQC values. The 10th percentile of DOC values in Ecoregions based on Oregon's data had a slightly higher median, but maintained more of the range of the IWQC values at the extreme low end of the distribution. The EPA-recommended estimates of DOC were intended to produce values with few over-estimates of IWQC values (left of the dashed 1:1 line) than the Ecoregion estimates using the

Oregon dataset (**Figure 41**). The similarity between EPA's recommended 10th percentile data and DEQ's estimated 10th percentile data provides strong evidence that DEQ may reliably derive estimates for parameters from its own database.

Figure 40: Comparison of measured (actual) and estimated chronic IWQC distributions from DOC estimates in EPA Level-III Ecoregions

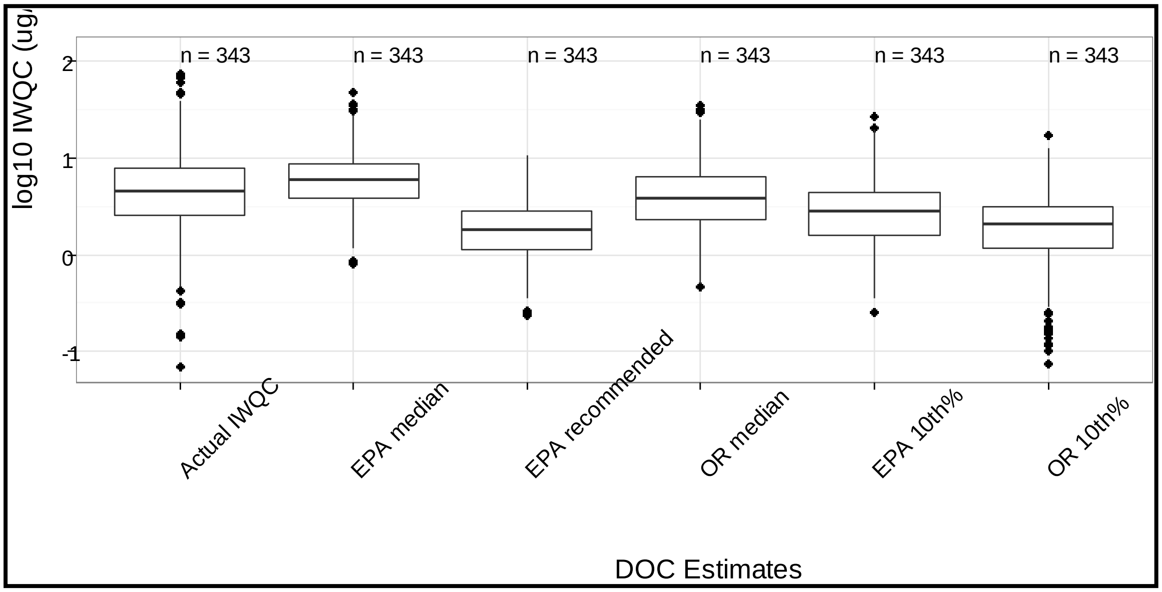
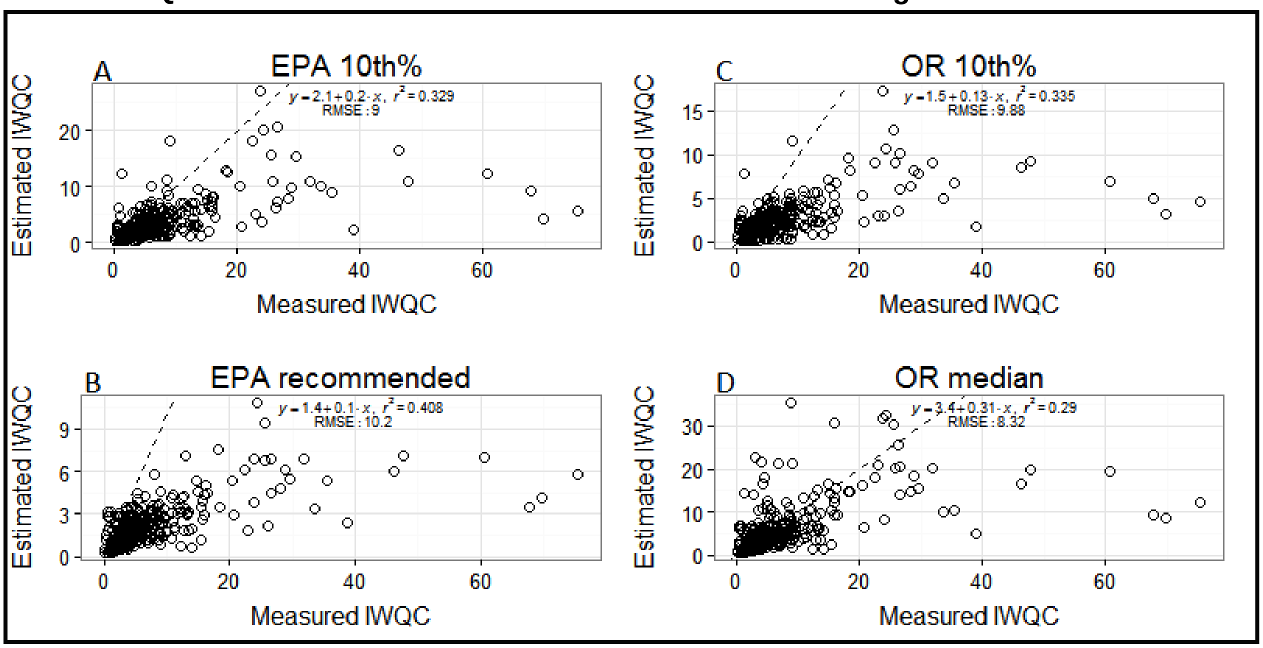


Figure 41: Regression relationships between measured chronic IWQC and estimated chronic IWQC from each of the DOC estimates in Level-III Ecoregions



DEQ compared DOC data aggregated over the EPA Level-III Ecoregions versus the DOC data aggregated over larger DEQ physiographic regions (**Figure 42**). The median IWQC values using EPA's recommended and 10th percentile estimates of DOC for Level-III Ecoregions tended to be about half of the respective median IWQC values generated using either the median or 10th percentile DOC estimates for the OR physiographic regions (**Table 28**).

Figure 42: Comparison of measured (actual) and estimated chronic IWQC distributions from DOC estimates in EPA Ecoregion and Oregon physiographic regions

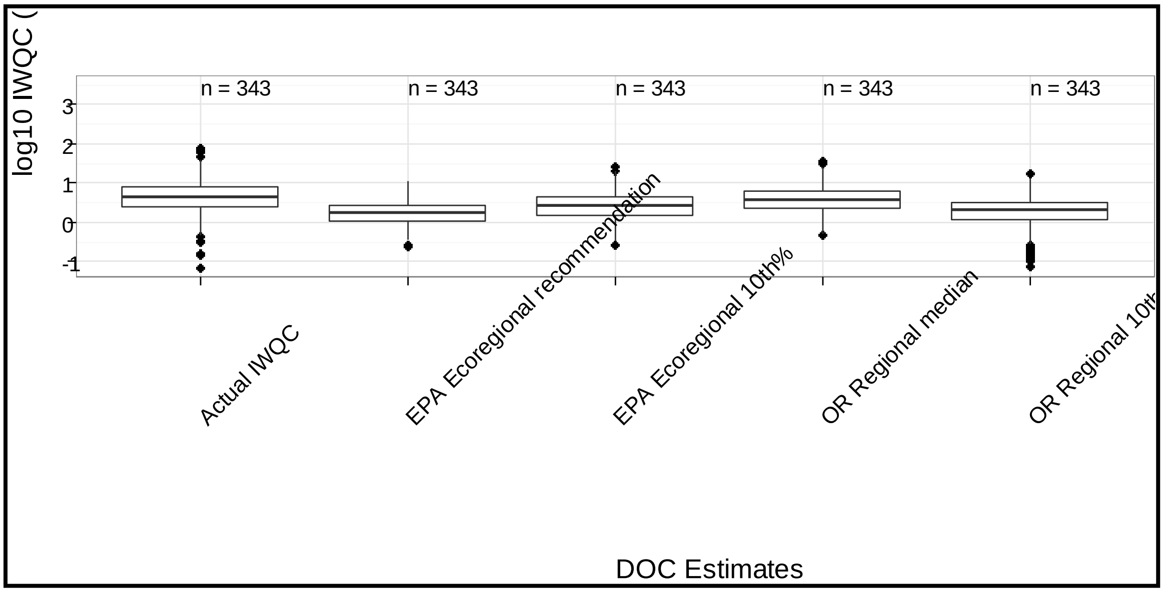


Table 28: Summary of differences in chronic IWQC from DOC estimates in EPA Ecoregion and Oregon physiographic regions

Estimation Method	Range	Median	CV
Measured	75.3	4.50	1.30
EPA 10th % (NOCD)	26.7	2.79	0.94
EPA Median (NOCD)	46.8	6.03	0.79
EPA Recommended (NOCD and WSA)	10.6	1.79	0.71
Oregon 10th %	17.1	2.08	0.87
Oregon median	34.9	3.89	0.98

Using 10th percentile estimates for DOC values is a conservative approach for determining protective copper criteria where DOC data are not available. Such a conservative approach may be appropriate for screening purposes. This approach requires that at least pH, temperature and specific conductance data are available in order to calculate an IWQC value using the BLM. Using EPA-recommended DOC concentrations assigned to sites based on Level-III Ecoregions appear to result in an unreasonably conservative approach. The range is smaller and the median IWQC is lower when calculated using the recommended DOC default estimated value for EPA Ecoregions versus the actual IWQC calculated from measured data (**Figure 42**). Using DEQ's 10th percentile data as the estimate is also a conservative approach. The potential for over-estimating the IWQC, resulting in potentially under-protective criteria being applied for a site (i.e. data points to the left of the dashed 1:1 line) appears to be greater when using the DEQ estimates (**Figure 41,** panel C,D), rather than the EPA estimates (**Figure 41,** panel A,B). There were 21 instances (6%) where IWQC calculated using the Oregon physiographic regional 10th percentile of DOC or the EPA's recommended 10th percentile DOC were greater than measured values. In contrast, there were 56 instances (16%) where the IWQC calculated from the EPA's Ecoregional 10th Percentile DOC (from the NOCD), were higher than the IWQC calculated using measured data. Either the EPA Recommended 10th Percentile values (NOCD + WSA data), or Oregon's 10th percentile of the Ecoregions appears to be equally conservative in this case.

VII.B Evaluation of Using Estimated pH and Temperature

The BLM parameters of pH and temperature are fundamental physical measurements of water chemistry. These measurements are time variable on diurnal, episodic, seasonal and annual timescales, and do not correlate well to specific conductance or other water quality parameters.

DEQ could not identify a commonly collected surrogate for estimating temperature at a site and did not investigate whether any other surrogate could be used to estimate temperature. In addition, temperature is not a particularly sensitive parameter in Oregon.

Alkalinity is a measure of the capacity of water to neutralize acid. The level of acid or base in water is measured by pH. Alkalinity and pH, along with temperature are used to determine the amount of inorganic carbon using equilibrium equations. There is normally a strong relationship between alkalinity, pH, and inorganic carbon. However, DEQ found that in its data set, there was not an empirical relationship that could be used to predict pH from ambient alkalinity measures. (**Figure 43**).

The EPA did not evaluate conservative pH values across Level-III Ecoregions in the same manner as DOC in their Estimating Missing Parameters document[64]. Instead, given the ease of collection and relative ubiquity of temperature and pH data in water quality monitoring, the EPA recommended using measured data of these parameters for BLM calculations.

Although both pH and temperature are widely collected throughout the state of Oregon, there may still be a need to estimate these parameters when data are insufficient. Caution must be exercised when estimating pH values, as due to the log scale of pH values, even small differences in pH represent a large change in the concentration of the parameter. Measurements of pH experience a wide range and high variation across regions and among stream types (**Figure 33** and **Figure 54**). Therefore, in the absence of pH and temperature data for sites requiring BLM calculations, the following options may be considered:

1) Use existing pH or temperature data from representative locations. Many long-term monitoring sites with pH and temperature are available.

[64] EPA (2012). Development of Tools to Estimate Water Quality Parameters for the Biotic Ligand Model. Office of Water. April 2012. **820R12008.**

2) Estimate a default value, similar to estimating a default DOC value, based on data from the Oregon database aggregated by physiographic region, as shown in **Table 29**, or Level III Ecoregion.

Figure 43: Regression relationship between pH and alkalinity for data collected in Oregon

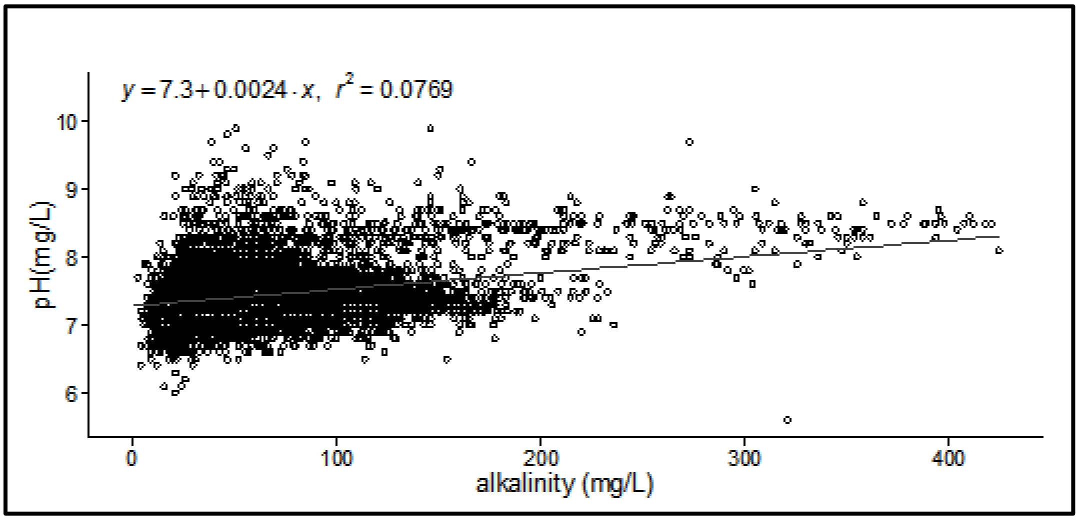


Table 29: DEQ physiographic region estimates of pH

DEQ Physiographic Region	pH	
	10th %	**Median**
Cascades	7.2	7.6
Coastal	7.1	7.6
Eastern	7.6	8.2
Willamette Valley	7.1	7.4

VII.C Evaluation of Using Regional BLM IWQC as Screening Level Water Quality Criteria for Locations Missing BLM Data

The second strategy for developing estimated copper criteria where DOC, pH, or conductivity data are incomplete or absent, relies on using IWQC developed from other sites with existing BLM data. This method uses the BLM outputs, or criteria, rather than estimating BLM input parameters to estimate criteria for sites with insufficient data. For example, a conservative percentile of measured IWQC could be used as screening level criteria for sites with insufficient BLM data. This strategy is particularly important for sites where copper ambient data are available, but BLM data are absent. DEQ anticipates this occurring as part of developing the Integrated Report for assessing Oregon waterbodies. DEQ evaluated two approaches for developing screening criteria: (1) statewide; and (2) regional criteria based on DEQ's four physiographic regions.

To calculate the different summary statistics of IWQC values for Oregon, DEQ prepared a large data set of all the available samples from the Oregon database with complete sets of measured parameters, and additionally, samples with at least DOC, pH, temperature and specific conductance data. Any missing measurements of the geochemical ions in a sample were estimated using the regression on specific conductance method described in section VI.A.1 from the equations in **Table 20**. Using this estimation approach to fill data gaps expanded the initial dataset of samples with a complete set of measured BLM parameters to a total of 4,607 samples to generate BLM IWQC. There were sufficient data to calculate IWQC values for 4,607 samples from 469 sites distributed across the state, with a median number of 19 samples per site (**Figure 44** and **Figure 45**).

Figure 44: Location and number of samples with sufficient data to calculate BLM IWQC

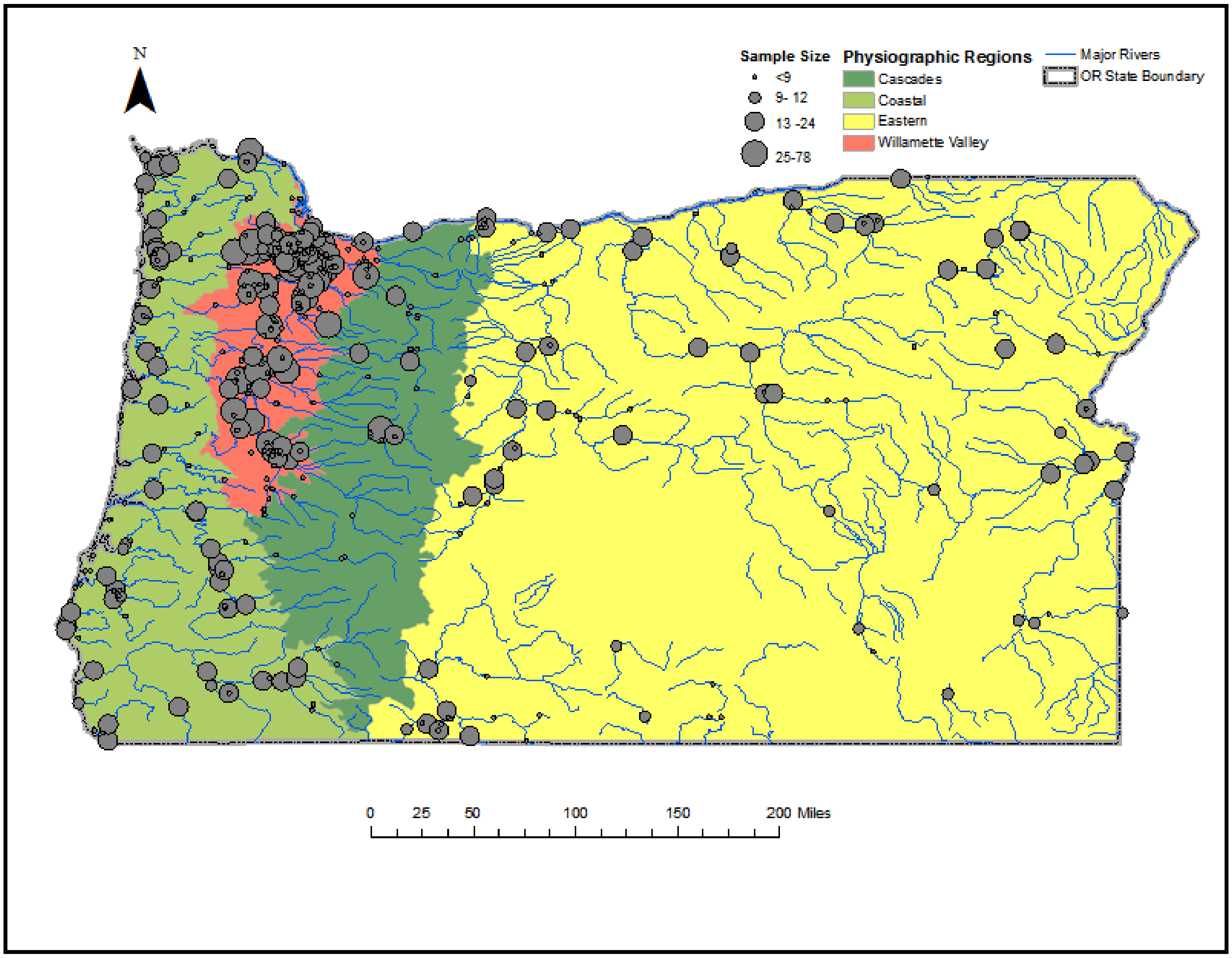
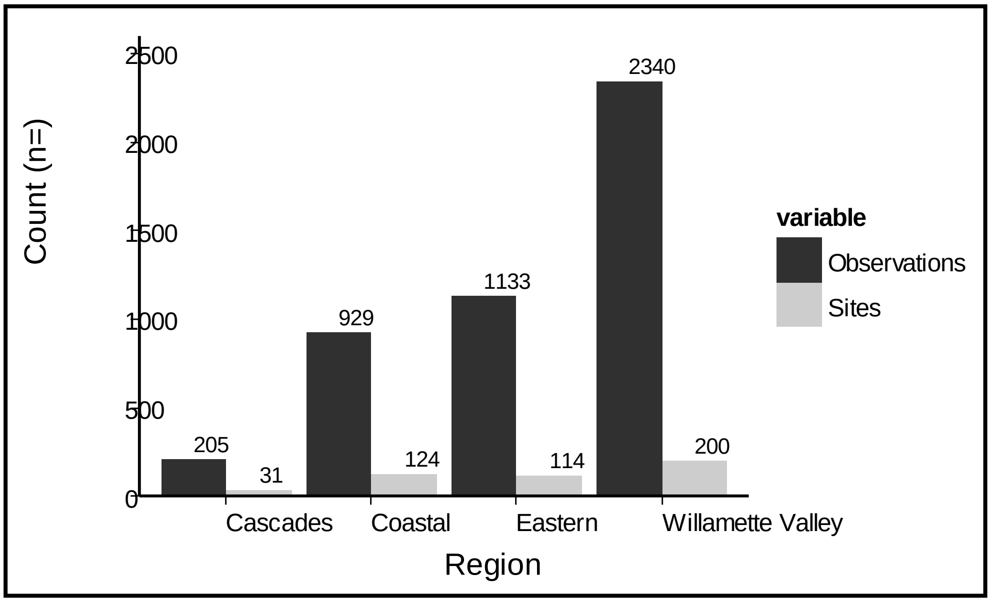


Figure 45: Number of samples per DEQ physiographic region.



DEQ examined the range, statistical distribution, and geographic distribution of the resulting IWQC values. The general distribution of IWQC values for the state is shown in a box-plot below (**Figure 46**, **Table 30)**. The dashed black lines represent various percentiles of the data. The red dashed lines indicate the median QL (2.0 µg/L) and DL (0.5 µg/L) for copper currently in the database (see section V.B.3). Chronic IWQC values ranged statewide from 0.70 µg/L to 434.3 µg/L, although these included some samples where the DOC was outside the calibrated range for the model. The median value was 5.16 µg/L. The 10^{th} percentile of chronic IWQC values was slightly below the median QL for copper concentrations. Distributions for subsets of the data, divided into data from the bottom 10^{th}, 50^{th} and 99^{th} percentiles of the whole database, are shown relative to the typical QL and DL for copper (from left to right, **Figure 47**).

Table 30: Default chronic IWQC values statistics for each physiographic region (as µg/L dissolved copper)

Region	n=	Min.	10th %	25th %	Median	CV
Cascades	205	0.13	0.28	0.86	1.82	0.85
Coastal	929	0.07	1.52	2.15	3.62	1.45
Eastern	1133	0.51	4.08	7.15	12.91	1.32
Willamette Valley	2340	0.07	1.88	2.74	4.6	1.15

Figure 46: Statewide distribution of IWQC results

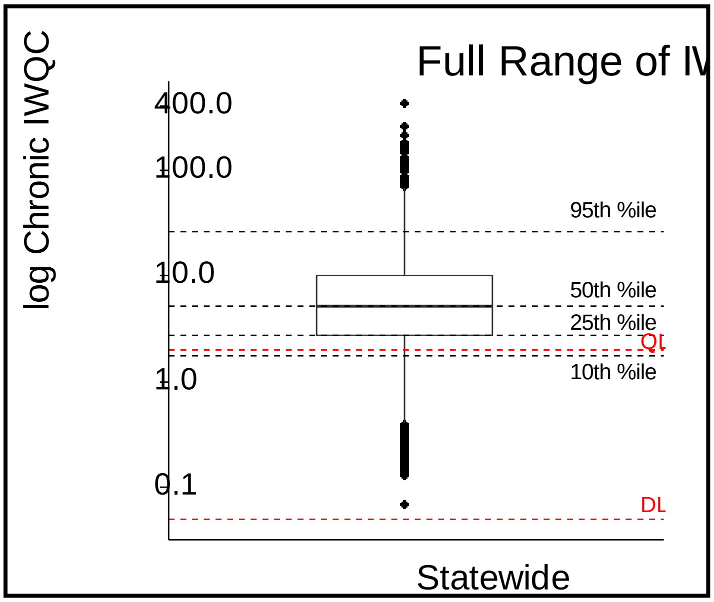
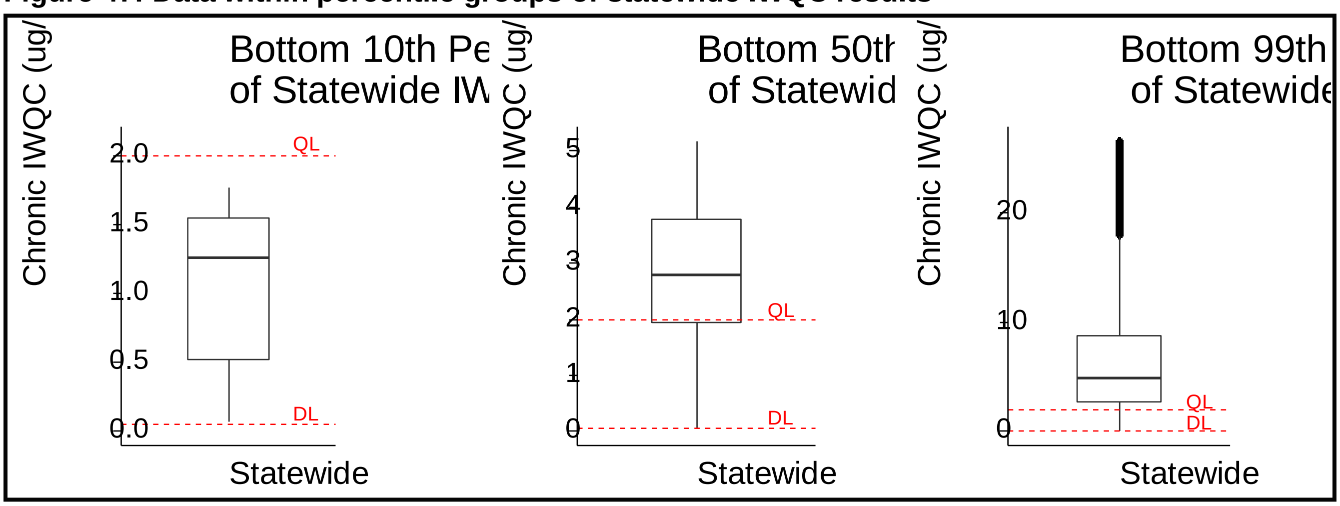
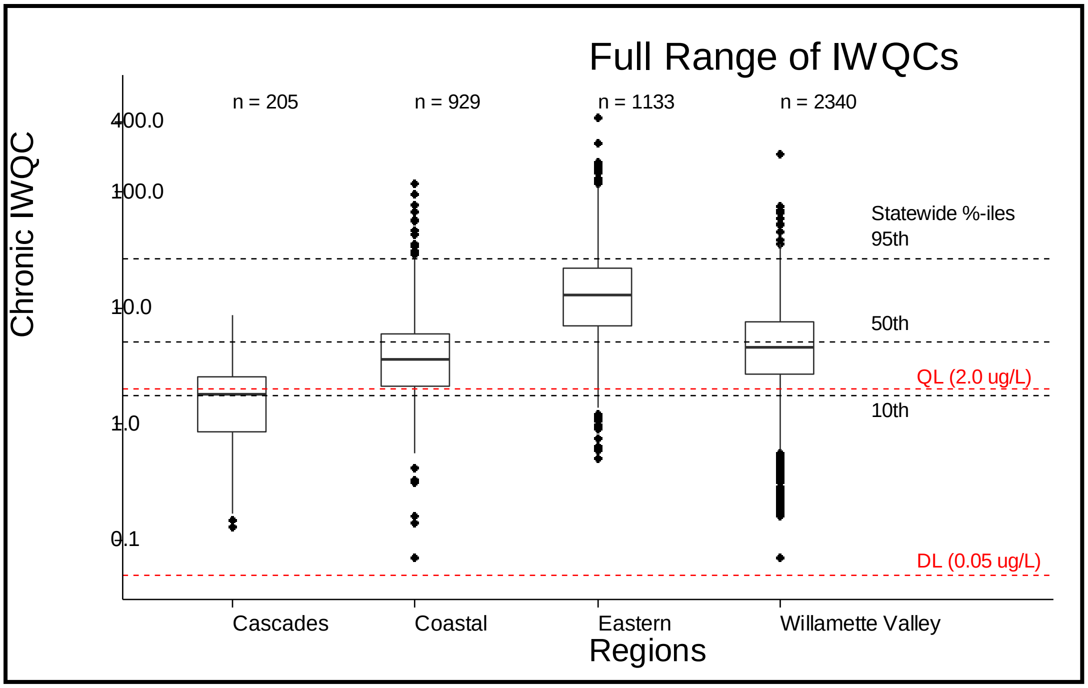


Figure 47: Data within percentile groups of statewide IWQC results



The IWQC distribution varied when samples were aggregated among different physiographic regions of the state (**Figure 48)**. The statewide 95th, 50th and 10th percentiles for all the data are shown using dashed black lines, and the typical QL and DL for copper are shown as dashed red lines. IWQC for the Cascade region were extremely low with the median IWQC value for sites within this area below the typical QL for copper. DOC data for the Cascade region as a whole were overall lower than other regions. The median IWQC increased for the Coastal region, Willamette Valley and Eastern regions respectively. These follow general trends for DOC, pH and specific conductance in these regions (see **Figure 32** and **Figure 33**, above). In general, the 25th percentile for each region was near or below the QL for copper (**Figure 47**).

Figure 48: Distributions of calculated IWQC by DEQ physiographic regions



IWQC values for Oregon showed a large range and varied considerably across the four physiographic regions of the state. The variability and range in BLM IWQC is tied to the corresponding range and variability of pH and DOC in each sample. In general, conservative lower quartiles for IWQC were near or below the QL used for copper samples available in the DEQ database. Any potential estimated BLM criteria applied statewide or regionally that are near or below QLs or DLs should be validated. Setting regulatory criteria at very low concentrations may be highly costly or unfeasible to obtain, and the ecological value of restricting criteria at these levels is uncertain. One approach for validation could be to require site-specific sampling of copper and BLM parameters where estimated criteria are below the QL.

In order to evaluate the relative impact of using BLM IWQC as screening level criteria to be applied at locations without sufficient BLM input data, DEQ analyzed the within-site variability of IWQC values for selected sites with at least 12 samples that had measured values for at least DOC, pH, temperature and specific conductance. **Figure 49** shows general patterns of within-site variability for the four sites with the longest data records of IWQC in each physiographic region. IWQC values for sites in the Cascades indicated chronic copper criteria in a narrow range of ~0.15 — ~4.2 μg/L. Sites in the Coastal region, Eastern, and Willamette regions displayed a wider range of IWQC values, and higher variability within sites. However, even within different regions, some sites displayed narrow ranges of IWQC (**Figure 49**, **Table 31)**. Data for sites in the Coast Range were generally available for larger river systems where the headwaters did not necessarily originate in the coast range itself. For example, the Columbia and Rogue Rivers, or Bear Creek, which receives water from the adjacent Klamath Basin via the Emigrant Reservoir, may not represent typical chemistry of coastal stream systems. Therefore, these results should be used for comparative purposes only, and some caution in extending these results to smaller coastal streams is warranted.

Figure 49: Within-site distribution of IWQC values for selected locations

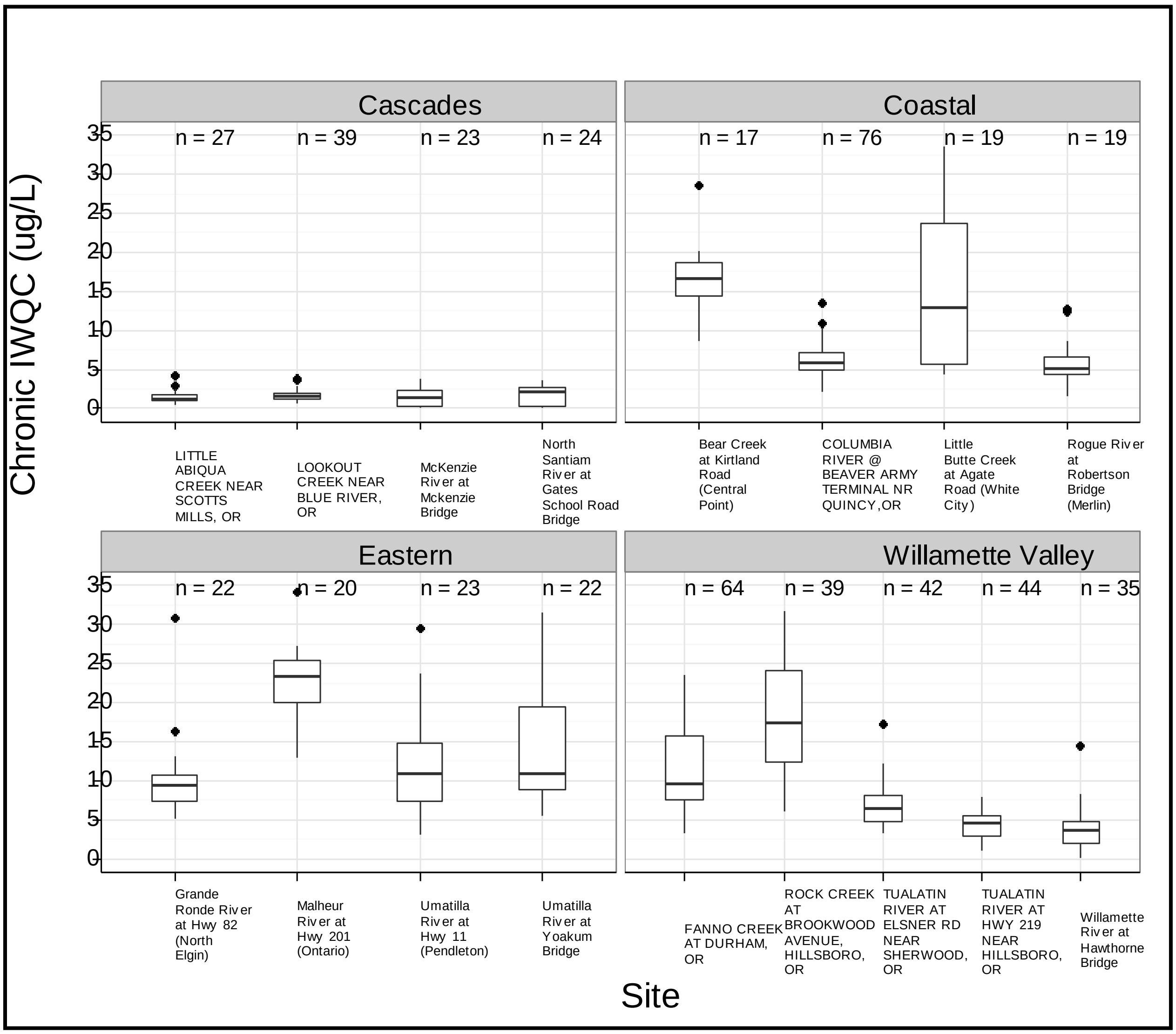


Table 31: Site-Specific chronic IWQC results for selected sites with at least 12 samples

Region	Regional 10th% Default	Regional Median Default	Site	n	Min	10th %	25th %	Median	Max
Cascades	0.3	1.82	McKenzie River	23	0.15	0.24	0.28	1.29	3.71
Cascades	0.3	1.82	North Santiam River	24	0.13	0.26	0.30	2.09	3.57
Cascades	0.3	1.82	Lookout Creek near Blue River	39	0.67	0.93	1.15	1.5	3.76
Cascades	0.3	1.82	Little Abiqua Creek	27	0.52	0.72	1.03	1.27	4.20
Coastal	1.5	3.62	Rogue River (Merlin)	20	1.53	3.64	4.38	5.255	43.30
Coastal	1.5	3.62	Little Butte Creek (White City)	19	4.27	4.56	5.65	12.82	33.59
Coastal	1.5	3.62	Bear Creek (Central Point)	19	8.54	12.45	14.59	17.02	77.10
Coastal	1.5	3.62	Columbia River (Quincy)	76	2.18	4.22	4.92	5.805	13.46
Eastern	4.1	12.91	Umatilla River at Yoakum Bridge	23	5.52	7.52	9.14	11.26	36.41
Eastern	4.1	12.91	Umatilla River (Pendleton)	23	3.00	6.66	7.29	10.9	29.58
Eastern	4.1	12.91	Malheur River (Ontario)	23	13.03	18.31	20.51	24.04	179.11
Eastern	4.1	12.91	Grande Ronde River (N. Elgin)	23	5.18	6.29	7.51	9.6	38.21
Willamette Valley	1.9	4.6	Willamette River at Portland	35	0.20	1.83	2.04	3.72	14.49
Willamette Valley	1.9	4.6	Tualatin River (Hillsboro)	44	1.08	2.41	2.89	4.6	7.85
Willamette Valley	1.9	4.6	Tualatin River (Sherwood)	42	3.21	3.80	4.67	6.365	17.28
Willamette Valley	1.9	4.6	Fanno Creek (Durham)	64	3.36	5.77	7.55	9.545	23.60
Willamette Valley	1.9	4.6	Rock Creek (Hillsboro)	40	6.07	10.41	12.37	17.785	45.92

VII.D Results Summary

- Oregon-estimated DOC values versus EPA-estimated DOC values for Level-III Ecoregions:
    - EPA's DOC database is weighted towards low DOC sites; is designed to provide conservative estimates (i.e.,10th percentiles) of DOC concentrations in each Ecoregion; and includes data from states other than Oregon. In contrast, Oregon DEQ's database is designed to capture a range of waters that better represent water chemistry conditions that will be encountered within the state.
    - For Level III Ecoregions, the DEQ estimates for median and 10th percentile DOC concentrations were generally lower than EPA's median and 10th percentile DOC concentrations.
    - There was closer agreement between IWQC estimated using DEQ and EPA Level-III Ecoregion IWQC estimates using the 10th percentile of DOC (root mean square error (RMSE) = 1.86 μg/L) than using the median DOC (RMSE = 3.76 μg/L).
    - The distribution of IWQC values calculated from EPA's Level-III Ecoregion DOC estimates tended to be slightly lower than IWQC generated from measured data.
    - When comparing DOC data aggregated over the nine EPA Level-III Ecoregions to the four DEQ physiographic regions, the IWQC estimates for the EPA Ecoregions are lower and have a narrower range than the estimates for DEQ's four physiographic regions (**Figure 42**).
    - The similarity between EPA's recommended 10th percentile data and DEQ's estimated 10th percentile data provides strong evidence that DEQ may reliably derive estimates for parameters from its own database.
- DEQ and EPA did not evaluate approaches for developing estimated pH or temperature estimate values for Level III Ecoregions. However, due to the ubiquity of monitoring sites containing pH and temperature data, on a case by case basis, Oregon may be able to use representative data from nearby monitoring locations for samples missing these parameters.
    - Given the insensitivity of the BLM to temperature, relevant seasonal or regional means may be adequate to provide estimates for this parameter without substantive bias in the derived IWQC.
- DEQ evaluated an approach that could be used to set conservative screening level criteria at sites without sufficient BLM data.
    - BLM IWQC vary widely across the state and within physiographic regions, hence, any particular estimation basis will carry a certain degree of error compared with IWQC based on measured values.
    - Both the median and 10th percentile of IWQC values statewide and for the four physiographic regions were near or below the average quantification limit (QL) for copper.
    - A conservative regional or statewide BLM IWQC may be used as an initial screening tool for locations without sufficient BLM data, but with dissolved copper data.
    - Using IWQC based on a regional estimate would yield some false positives, or exceedances, while the measured BLM IWQC would not.
    - When available, measured IWQC values should supersede estimated IWQC when assessing compliance with copper criteria.

VIII. Biotic Ligand Model Results and Comparisons

VIII.A Objectives

The objectives of this section are to generally compare BLM criteria to the currently effective hardness-based criteria and determine water quality criteria exceedances based on ambient copper concentrations in Oregon. Specifically, the objectives of this evaluation are to:

- Examine the long-term variability of DOC, pH, and hardness-based and BLM-derived IWQC at representative locations to evaluate the applicability of criteria over time.
- Evaluate the effect of using estimated DOC and pH values based on regional or statewide data as inputs to the BLM in order to estimate IWQC for locations where sufficient measured data for these parameters are not available. Generate IWQC for all sites that have at least measured pH and DOC data. Missing geochemical ions and alkalinity data are estimated using specific conductance data as describe in section VI.A.1.
- Evaluate the range and distribution of BLM IWQC.
- Evaluate the effect of using different statistical summary values of pooled IWQC data, such as percentiles or medians, to develop statewide or regional screening criteria for locations where there are not sufficient BLM data available.

VIII.B Comparison of BLM Criteria and Hardness-Based Criteria

VIII.B.1 BLM Criteria and Hardness-Based Criteria

The Complete Measured Database (Appendix A) used to evaluate model sensitivity and estimation methods also provides a means to compare the differences in potential copper IWQC derived from the BLM with Oregon's currently effective hardness-based criteria (HBC). Specifically, DEQ analyzed how the magnitude of these criteria differs, and under what conditions the hardness-based criteria might be underprotective compared to the BLM criteria.

The hardness-based criteria function as performance-based standards (equations) that calculate the expected acute and chronic toxicity of copper based on the hardness of a water sample (**Table 32**). According to EPA's 2007 Aquatic Life Ambient Criteria for Copper, the instantaneous criteria generated by the BLM for a given sample are assumed to provide a more accurate estimation of the toxic limit of copper than the hardness-based method it replaces. A comparison of the criteria derived by these two methods is shown in **Figure 50** and **Figure 51**. HBC are plotted on the x-axis, and the BLM IWQC are plotted on the y-axis. The dashed black line is the 1:1 line where the HBC for each sample are equal to the IWQC. Values above the 1:1 line show where BLM criteria are higher (less stringent) than HBC. Values below the 1:1 show where BLM criteria are lower (more stringent) than HBC. The dashed red lines indicate acute and chronic copper criteria proposed by the National Marine Fisheries Service (NMFS) in their biological opinion for Oregon[65]. The proposed criteria are 1.45 μg/L (chronic) and 2.3 μg/L (acute)[66].

Table 32: Currently effective hardness-based copper criteria

Effective Oregon Aquatic Life Criteria for Copper (OAR 340-041-8033, Table 30, as total recoverable copper)	
Chronic	CCC = (exp(0.8545*ln[hardness] -1.465))
Acute	CMC = (exp(0.9422 *[ln(hardness)] -1.464))

[65] National Marine Fisheries Service. Jeopardy and Destruction or Adverse Modification of Critical Habitat Endangered Species Act Biological Opinion for Environmental Protection Agency's Proposed Approval of Certain Oregon Administrative Rules Related to Revised Water Quality Criteria for Toxic Pollutants. NMFS Consultation Number: 2008/00148. August 14, 2012. The jeopardy decision also included acute and chronic freshwater criteria for ammonia and aluminum, and the freshwater acute criterion for cadmium.

[66] National Marine Fisheries Service. Jeopardy and Destruction or Adverse Modification of Critical Habitat Endangered Species Act Biological Opinion for Environmental Protection Agency's Proposed Approval of Certain Oregon Administrative Rules Related to Revised Water Quality Criteria for Toxic Pollutants. NMFS Consultation Number: 2008/00148. August 14, 2012.

Figure 50: Comparison of hardness-based and BLM derived chronic criteria

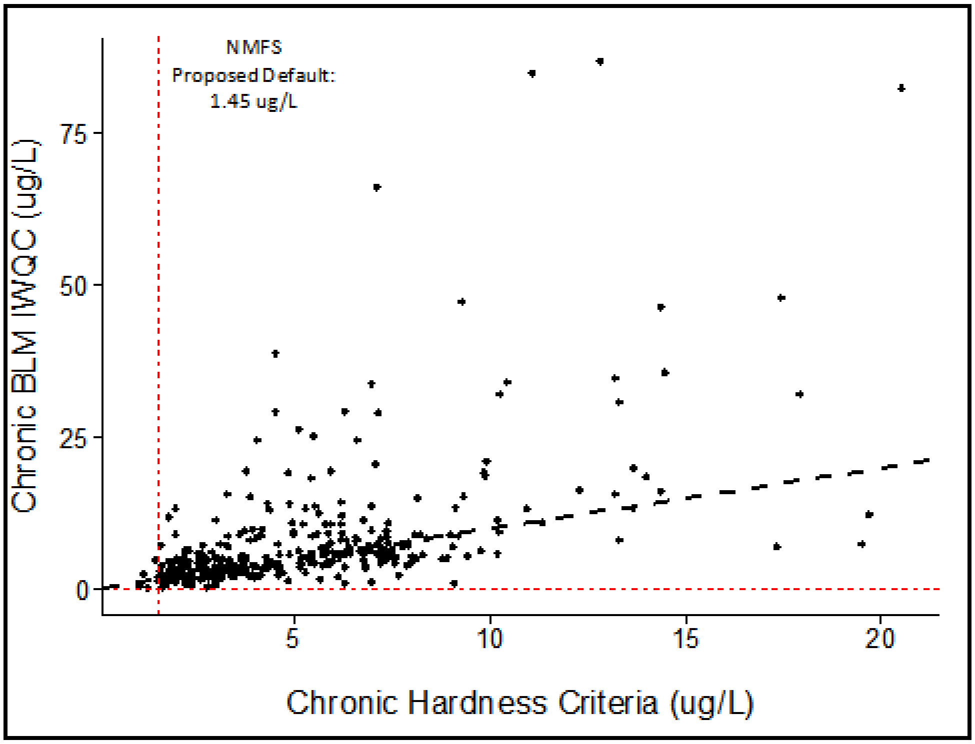
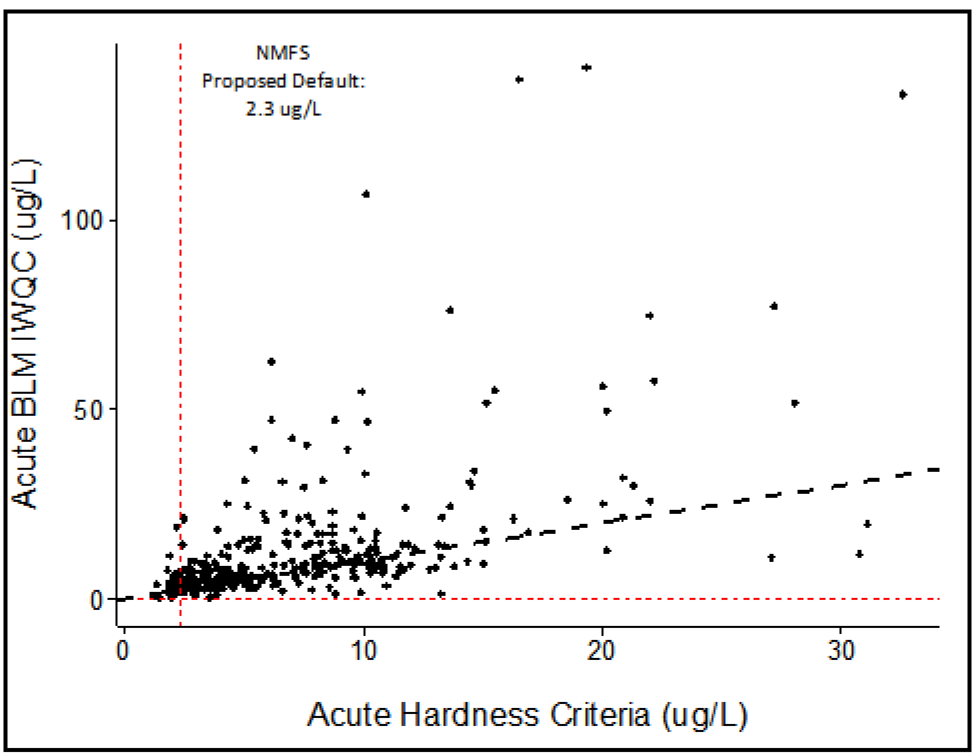


Figure 51: Comparison of hardness-based and BLM derived acute criteria



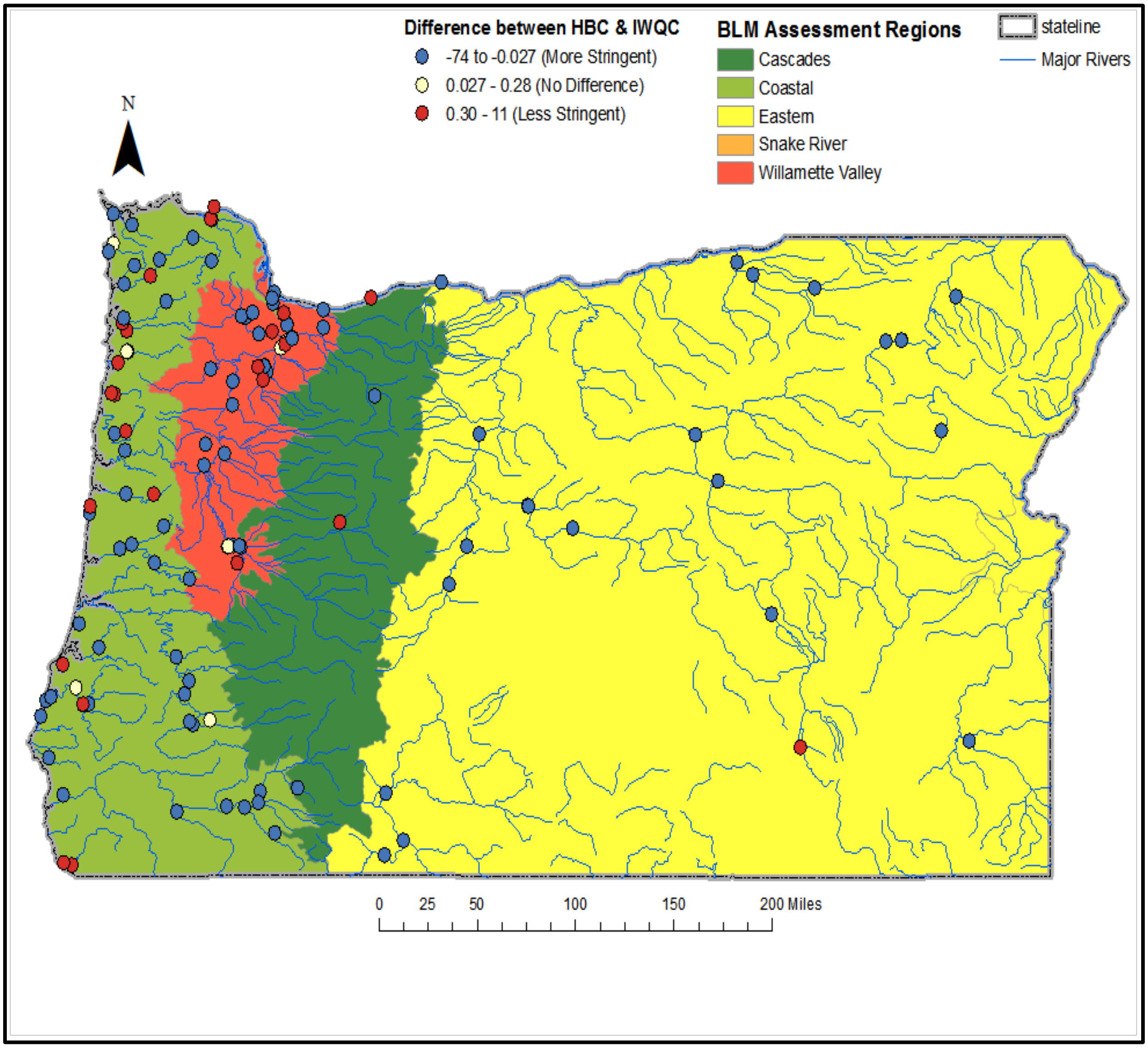
In general, the dissolved criteria calculated using the BLM were higher, or less stringent, than the total recoverable criteria calculated using the hardness based criteria. It is reasonable to expect that the dissolved concentration of copper is a lower proportion of the total recoverable concentration. There were 342 samples that had measured values for all BLM parameters and hardness data. There were 178 samples (or 52%) that had HBC > BLM IWQC. Because of the substantial amount of information indicating that the BLM is more representative of the chemical conditions contributing to copper toxicity, the HBC related to these samples could be under-protective of aquatic life. There were 164 samples (48%) that had HBC < BLM IWQC, and could be considered too conservative. A comparison of the sample medians for parameters at these sites is in **Table 33**. There were statistically significant differences between the median DOC, pH and sodium for sites where HBC > IWQC. In each case, the medians for these parameters were lower than the median of the entire population. Samples with low relative DOC and pH may be strong indicators of conditions where copper criteria will be lower in order to protect aquatic life.

Figure 52 shows the location of sites where the difference between the HBC and IWQC is positive (i.e. less stringent, red circles), where the HBC ≈ IWQC (i.e. no difference, yellow circles) and where the HBC and IWQC is negative (i.e. more stringent, blue circles). There was a higher frequency of sites where the HBC would be considered less protective than the BLM in the Coast Range and Willamette Valley physiographic regions.

Table 33: Comparison of parameter medians for sites where hardness-based criteria are less stringent relative to the BLM

	HBC < IWQC (HBC protective)	HBC > IWQC (HBC not protective)	Kruskal-Wallis test
Parameter	**Sample median (mg/L, except pH)**		**p-value**
Hardness	39.98	39.24	NS
DOC	3.36	1.56	<0.001
pH	7.7	7.4	<0.001
Alkalinity	44.82	37.32	NS
Sodium	8.29	5.75	<0.05
Calcium	9.73	9.94	NS
Potassium	1.51	0.99	NS
Magnesium	3.80	3.49	NS
Chloride	6.16	4.98	NS
Sulfate	4.92	6.02	NS

Figure 52: Sites where at least one sample of the hardness-based criteria are less stringent than the BLM IWQC



VIII.B.2 Temporal Variability of BLM and Hardness-based Criteria

Because DOC and pH are very sensitive parameters in the BLM, DEQ examined whether we could observe trends in seasonal or shorter temporal variability scales at sites with long-term monitoring records. DEQ also included hardness, so that we could compare variability in DOC, pH and hardness parameters, and the resulting differences between BLM criteria and hardness-based criteria. By examining seasonal and temporal trends in each of the four physiographic regions, DEQ evaluated whether increased monitoring to capture these variations is warranted. In addition, DEQ also evaluated whether large fluctuations in these parameters would lead to corresponding differences in the resulting BLM criteria over time.

DEQ selected a subset of ten sites with records of at least 24 consecutive monthly samples[67] of pH, DOC, temperature and specific conductance measured as specific conductance. Sixty-three out of 145 sites with a long-term data record of at least nine samples were located in the Willamette Basin. DEQ selected at least two sites with the longest records from each physiographic region.

DOC Variability

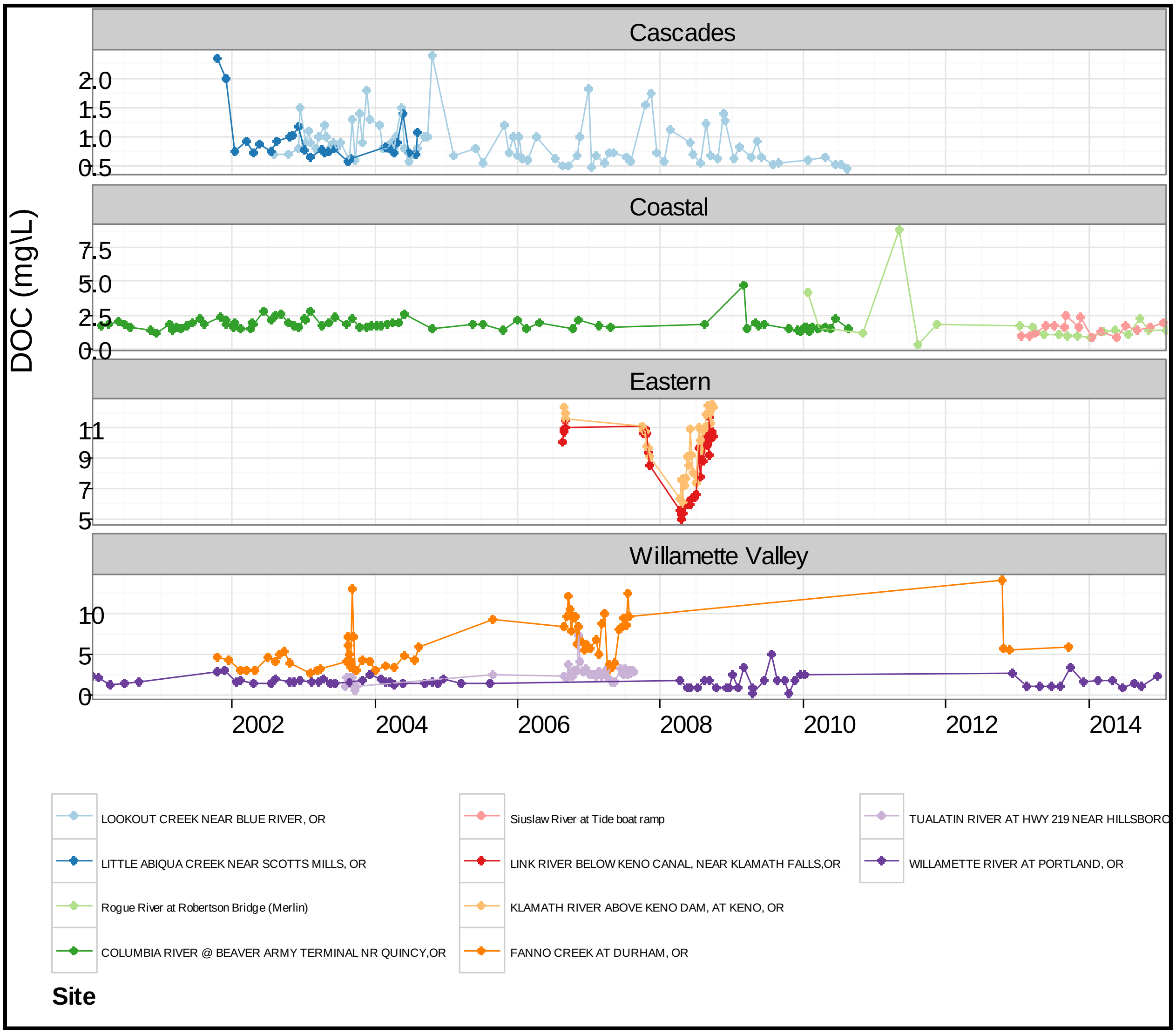
The examples include both larger rivers and smaller tributaries, and do not necessarily represent typical or average conditions for the region. **Table 34** shows the sampling locations selected, their region, stream order and size of area drained at the site, and statistics on the variability of data in the time series. The coefficient of variation (CV) provides a basis for comparing the variability around the mean in each time series. A higher CV value indicates more variability in a data set. These sites are shown from top to bottom in **Figure 53.**

Table 34: Summary of variability in DOC time series

Region	Site	Stream Order	Drainage Area (km^2)	Range (mg/L)	median DOC (mg/L)	CV
Cascades	Lookout Creek near Blue River, OR	3	63	1.95	0.8	0.40
Cascades	Little Abiqua Creek near Scotts Mills, OR	2	25	1.76	0.79	0.43
Coastal	Rogue River at Robertson Bridge (Merlin)	6	8,556	8.44	1.39	0.99
Coastal	Columbia River @ Beaver Army Terminal near Quincy, OR	9	619,784	3.55	1.77	0.26
Coastal	Siuslaw River at Tide boat ramp	5	1,545	1.7	1.5	0.33
Eastern	Link River below Keno Canal, near Klamath Falls, OR	1	4	6.7	9.4	0.26
Eastern	Klamath River above Keno Dam, at Keno, OR	1	4	6.5	10.4	0.19
Willamette Valley	Fanno Creek at Durham, OR	3	82	11.6	5.4	0.47
Willamette Valley	Tualatin River at Hwy 219 near Hillsboro, OR	5	1,196	6.8	2.4	0.42
Willamette Valley	Willamette River at Portland, OR	7	28,921	4.9	1.6	0.47

[67] Additional long-term data for the Tualatin Basin and Willamette Valley, including Fanno Creek and the Tualatin River, were provided by Clean Water Services, Hillsboro, OR.

Figure 53: Long-term DOC concentration time series for 10 Oregon water bodies across four physiographic regions



In **Figure 53**, DOC appears to be low and relatively stable over time in the small stream evaluated in the western Cascades. Large, high-order rivers, such as the Columbia (green, 2nd panel from top) and Willamette Rivers (purple, 4th panel from top) are also relatively low in DOC concentration and appear stable over time.

Tributary streams in the Willamette and Coastal physiographic regions, such Lookout Creek, the Siuslaw River, and Fanno Creek (**Figure 53**, 1st, 3rd, and 4th panels from top) showed higher variability in DOC concentration. DOC concentrations may vary over time in tributary streams as a function of space, time, natural background, or many other different internal and external variables.

pH Variability

DEQ showed in section V.C.1 that the BLM is sensitive to variations in pH across Oregon. Measurements of pH values can vary considerably on multiple time scales and may exhibit high variability on diurnal, monthly, seasonal and inter-annual scales. BLM criteria tend to increase along with increasing pH values and generally, pH values for large rivers and small tributaries tend to fall into a similar range of values. In the Eastern arid physiographic region of the state, pH values for streams shown tended to be 1 to 2 units higher than values in the Cascades, Coastal and Willamette physiographic regions. This region is arid. The higher pH values in the example streams reflect a considerably higher level of alkalinity.

Figure 54: Long-term pH time series For 10 Oregon water bodies across four physiographic regions.

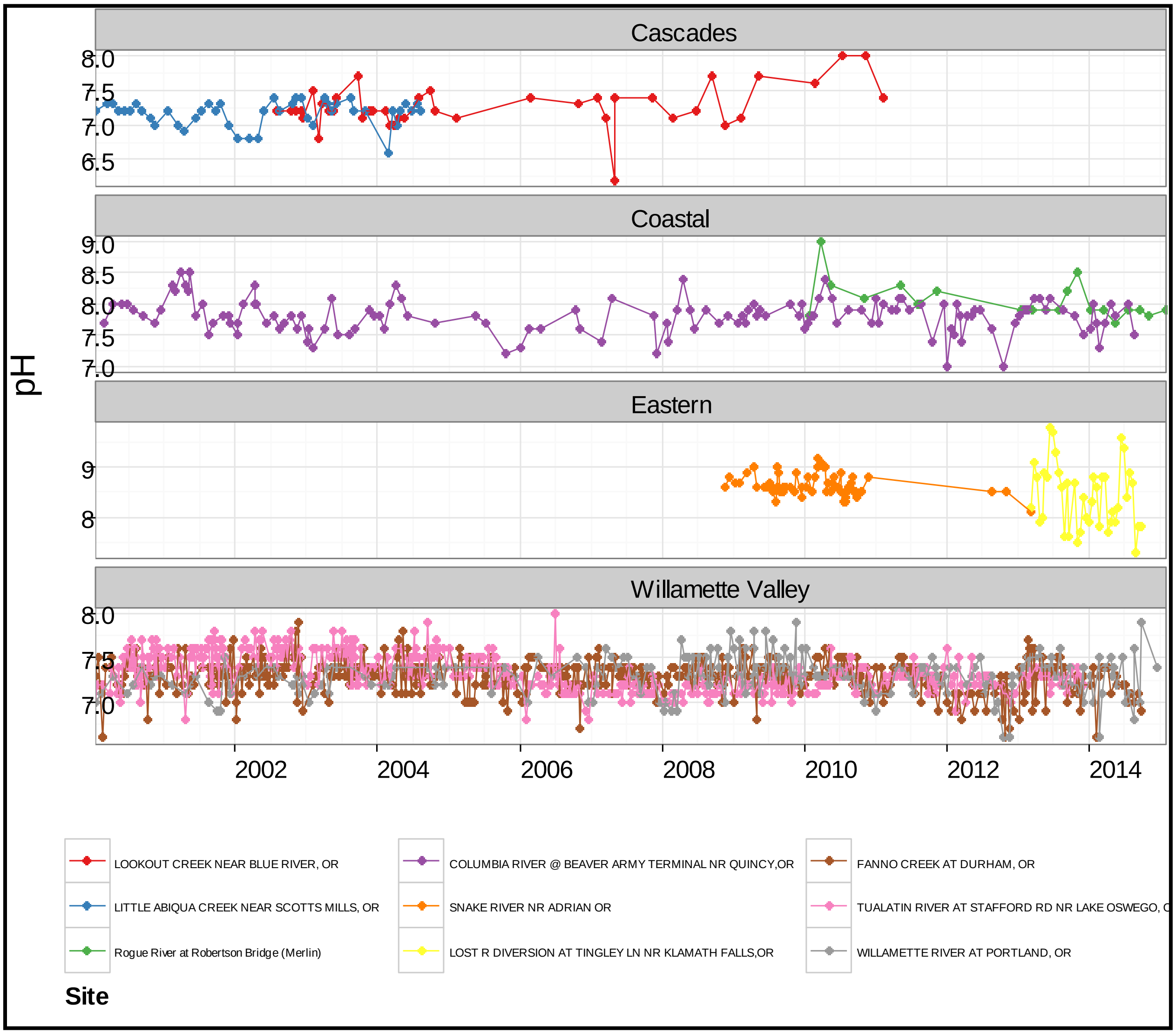


Table 35: Summary of variability in pH time series

Region	Site	Stream Order	Drainage Area (km^2)	Range pH	median pH	CV
Cascades	Lookout Creek near Blue River, OR	3	63	1.8	7.2	0.04
Cascades	Little Abiqua Creek near Scotts Mills, OR	2	25	0.80	7.2	0.03
Coastal	Rogue River at Robertson Bridge, Merlin, OR	6	8,556	1.3	7.9	0.04
Eastern	Columbia River @ Beaver Army Terminal near Quincy,OR	9	619,784	1.5	7.8	0.03
Eastern	Snake River near Adrian, OR	7	81,619	1.1	8.6	0.02
Willamette Valley	Lost River diversion at Tingley Ln. near Klamath Falls, OR	1	4.16	2.5	8.4	0.08
Willamette Valley	Fanno Creek at Durham, OR	3	82.14	1.3	7.3	0.02
Willamette Valley	Tualatin River at Stafford Rd. near Lake Oswego, OR	5	1,814	1.2	7.3	0.03
Willamette Valley	Willamette River at Portland, OR	7	28,921	1.3	7.3	0.03

Hardness Variability

There were not sufficient hardness data available to attain 24 consecutive monthly samples for all of the example streams. However, there were at least 12 consecutive monthly samples available for some of the streams used in **Figure 55** and **Table 36**. Hardness showed a similar spatial pattern to DOC with large, high-order streams and rivers, or sites from relatively un-impacted regions, such as the Cascades physiographic region, showing lower concentrations and low variability in hardness. Sites located in the Eastern region or on smaller tributaries in more developed areas, such as the Willamette physiographic region, showed higher concentrations and more variability for hardness.

Figure 55: Long-term hardness time series for six Oregon water bodies across four physiographic regions

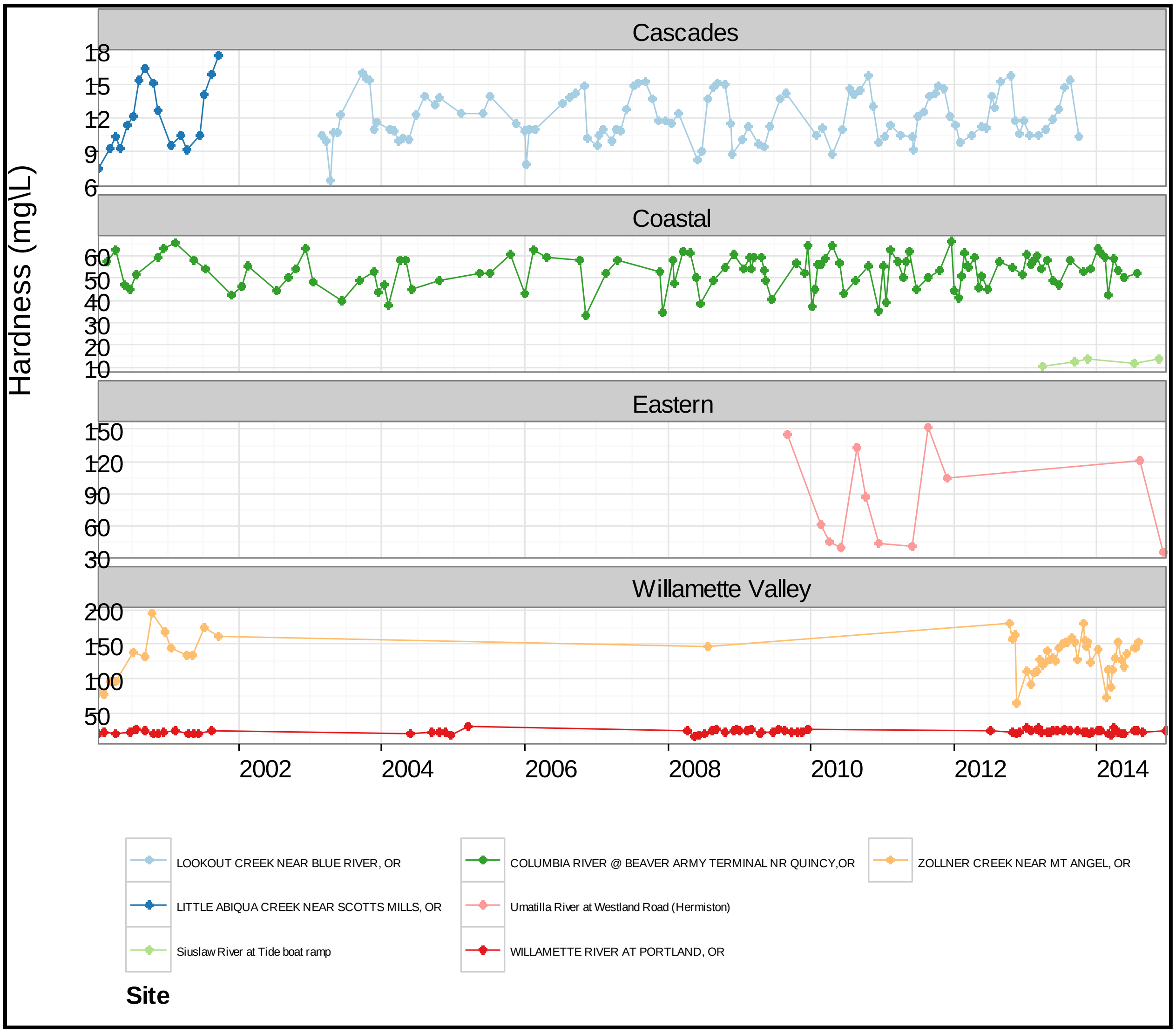


Table 36: Summary of variability in hardness time series

Region	Site	Stream Order	Drainage Area (km^2)	Range (mg/L)	Median Hardness (mg/L)	CV
Cascades	Lookout Creek near Blue River, OR	3	63	9.5	11.5	0.17
Cascades	Little Abiqua Creek near Scotts Mills, OR	2	25	9.99	11.3	0.25
Coastal	Siuslaw River at Tide boat ramp	5	1,545	3.3	12.4	0.10
Coastal	Columbia River @ Beaver Army Terminal nr Quincy, OR	9	619,784	33	53.9	0.14
Willamette Valley	Umatilla River at Westland Road (Hermiston)	6	5,465	116.4	74.1	0.54
Willamette Valley	Willamette River at Portland, OR	7	28,921	16	23.0	0.11
	Zollner Creek near Mt. Angel, OR	3	40	128	135.0	0.21

Figure 56: Comparison of chronic hardness-based and BLM criteria

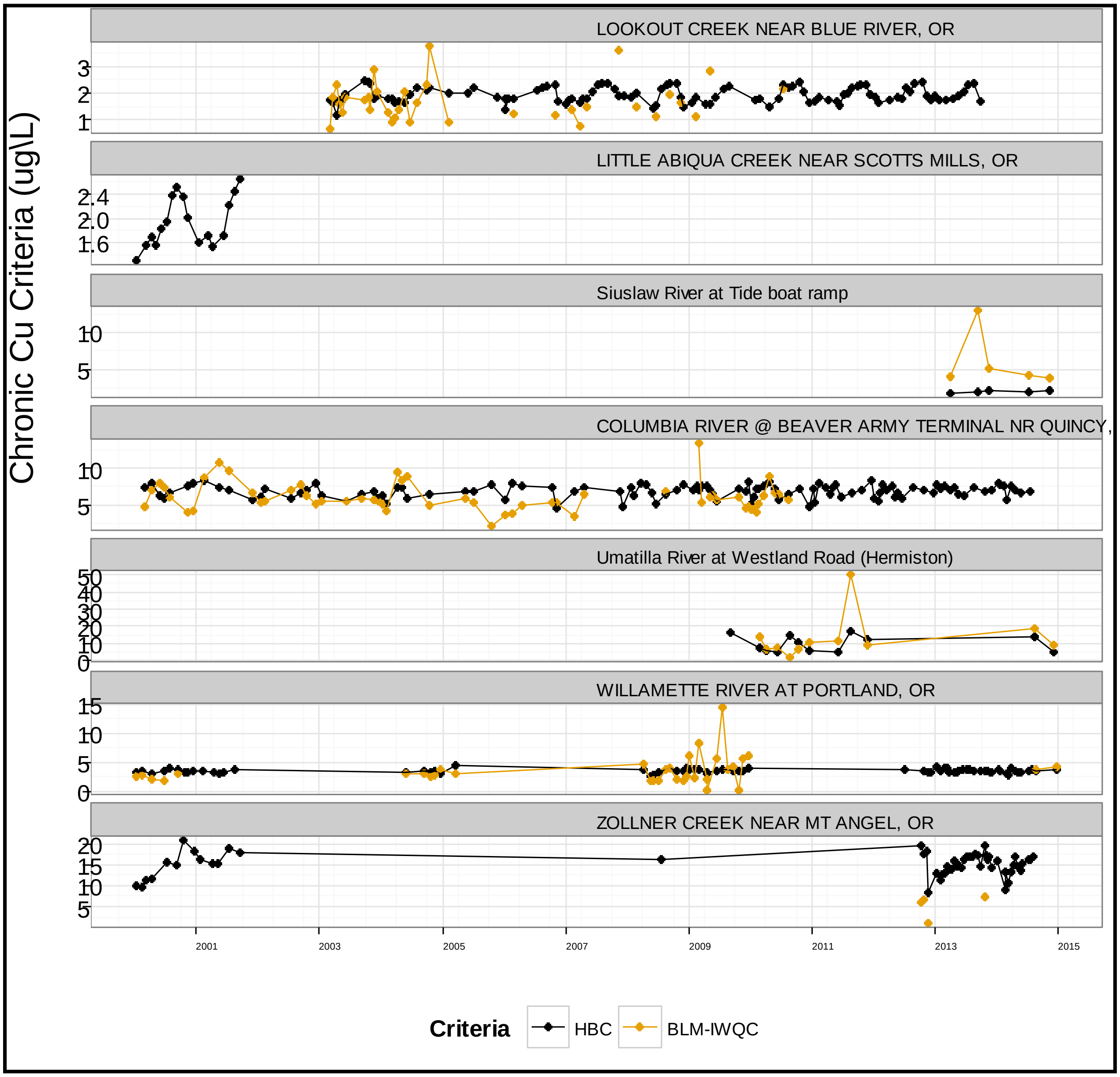


Table 37: Summary of variability comparing BLM-IWQC and hardness criteria time series

		Hardness-Based Criteria		BLM-IWQC	
Region	**Site**	**median**	**CV**	**median**	**CV**
Cascades	Lookout Creek near Blue River, OR	1.8	0.15	1.5	0.44
Cascades	Little Abiqua Creek near Scotts Mills, OR	1.8	0.21	NA	NA
Coastal	Siuslaw River at Tide boat ramp	1.9	0.09	4.2	0.65
Coastal	Columbia River @ Beaver Army Terminal near Quincy,OR	6.8	0.12	5.7	0.32
Eastern	Umatilla River at Westland Road (Hermiston)	7.8	0.47	9.3	0.99
Willamette Valley	Willamette River at Portland, OR	3.4	0.11	3.0	0.66
Willamette Valley	Zollner Creek near Mt Angel, OR	18.5	0.33	6.3	0.52

DEQ compared sites with long records of instantaneous hardness-based criteria to calculations of BLM IWQC with corresponding records of measured hardness, DOC and pH data (**Figure 24, Table 37**). We present chronic criteria, as opposed to acute criteria, as they are typically the most limiting water quality criteria for copper in Oregon. For most sites, there was not a sufficient number of measured BLM parameter values to calculate a long time series corresponding to available hardness data (see **Figure 56**, 2nd panel from top, Little Abiqua Creek, and 6th panel from top, Zollner Creek). For sites with a long, concurrent data record for both the hardness-based criteria and the BLM IWQC, both criteria values tended to be within the same order of magnitude, but the coefficient of variation for each stream was higher for BLM IWQC than hardness-based criteria. FMBs that account for time variability in IWQC may be a good approach for establishing prospective monitoring benchmarks for sites with sufficient data records.

The general relationship between hardness-based criteria and BLM IWQC within streams did not appear to differ between large, high-order rivers or smaller tributaries, and variability within sites was relatively low. Sites with high DOC samples also saw increases in the BLM IWQC that were not matched by fluctuations in the associated hardness-based criteria (**Figure 56**, 5h panel from top, Umatilla R.). Note that even though the BLM IWQC were frequently higher than the HBC, the minimum criterion value in each site was also defined by the BLM, which at times could be extremely low.

VIII.C Comparison of Copper Concentrations and BLM IWQC Values

Of the 4,607 samples with sufficient BLM parameters to calculate IWQC, there were 1,630 samples that also had concurrent dissolved or total copper data. DEQ calculated the ratio of copper concentration to the chronic BLM IWQC value to determine where copper concentrations were close to or exceeded the BLM IWQC criteria (**Figure 57**). These are expressed as chronic toxic units (CTUs), where a CTU of 1 indicates that dissolved copper concentration in a sample is equal to the IWQC, an CTU<1 indicates a copper concentration is below the criteria, and CTU >1 indicates copper concentrations in excess of the criteria. The value of CTUs indicates the relative proportion of copper concentration to its associated criteria. Since there are often multiple samples at each site, the maximum value of CTUs is displayed. Sites that are grey do not have any CTUs above 1, indicating that all copper concentrations were below the chronic IWQC value. Sites with larger circles and are green, orange, or red have CTUs > 1, indicating increasing disparity between the copper concentration and the IWQC. Each region has a site with at least one exceedance, where CTU > 1. The greatest number and severity of BLM IWQC exceedances occur in the Willamette basin, where a majority of NPDES dischargers are located (**Table 38**). Some locations had maximum copper concentrations 15-45 times higher than the chronic IWQC for the same sample. Seven percent of the samples in the Cascade region exceeded their sample specific IWQC. Some of these sites are quite geographically high in watersheds, but the exceedances were not as large as seen in lower geographic sites, such as in the Willamette region.

Figure 57: Locations where copper concentration exceeds IWQC

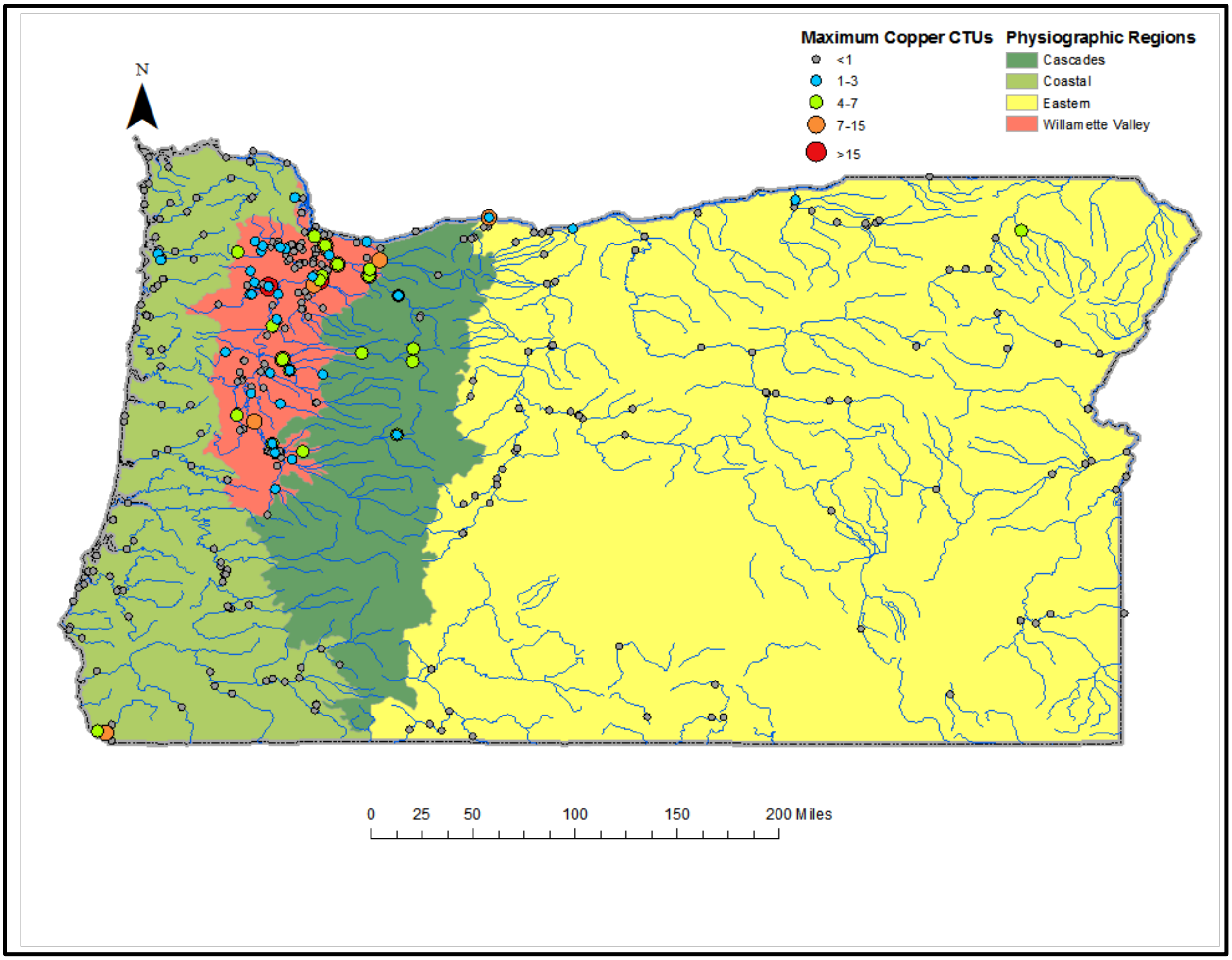


Table 38: Number of dissolved copper samples exceeding IWQC per region

Region	Samples (n)	Exceedances	%
Cascades	205	15	7.3
Coastal	929	5	0.5
Eastern	1133	8	0.7
Willamette Valley	2340	64	2.7
Total	4607	92	2.0

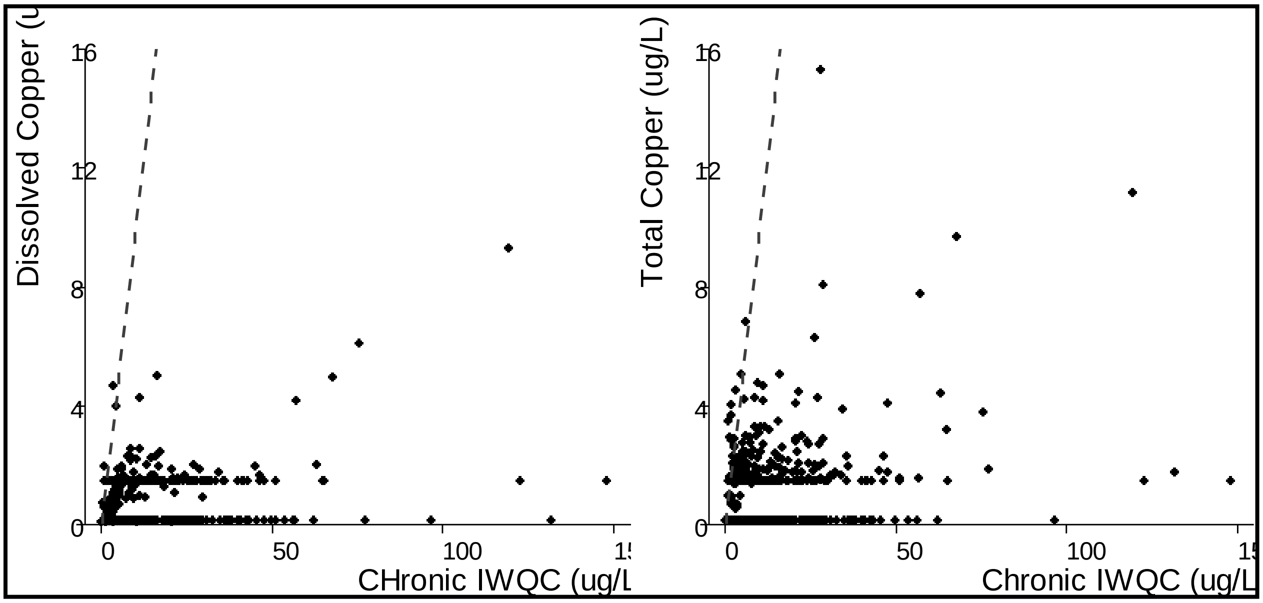
VIII.C.1 Evaluation of Paired Total and Dissolved Copper Data

DEQ noted in section V.B.5 that there were often disparities between the total and dissolved concentration of copper within the same sample, due to a combination of differential partitioning between particulates and dissolved copper, and to biases introduced by measurement error, potential contamination, and high detection limits relative to concentration. Since total metals data were collected more frequently than dissolved, DEQ examined sites with paired total and dissolved copper data to determine whether using measurements of either the total or dissolved form would be more likely to exceed the IWQC. There were 1,293 samples in the Oregon database with measurements of both total and dissolved copper, as well as sufficient BLM parameter data to calculate an IWQC for these samples **(Table 39**). Plots of copper concentration relative to chronic IWQC are show below (**Figure 58**). The 1:1 line, where chronic IWQC equals dissolved copper, is shown as a dashed line.

Table 39: Number of total, dissolved, and paired copper samples

Parameter	Samples (n)
Total Copper	3,565
Dissolved Copper	1,486
Paired Total and Dissolved	1,293

Figure 58: Paired dissolved and total copper concentrations versus chronic BLM IWQC



A Plot of the chronic toxic units (CTUs), the ratio of IWQC to total or dissolved copper concentration, where values less than 1 are meeting the IWQC, and values greater than 1 are exceeding the IWQC, is show below (**Figure 59**). Samples where the total and dissolved copper concentrations are equal, often when both are reported at the detection limit, is evident. The dashed lines are where CTUs are equal to one (i.e. where copper concentration equals the IWQC). Data points in the lower left quadrant represent samples where both total and dissolved copper concentrations are less than the IWQC and meet the criteria for those samples. Points in the upper right quadrant represent samples where both total and dissolved samples are greater than the IWQC. Points in the upper left quadrant, represent false positives, where the dissolved, but not the total copper concentration, are greater than the IWQC. The lower right quadrant represents false positives where the total copper, but not the dissolved copper, was greater than the IWQC.

Figure 59: Paired dissolved and total copper chronic toxic units

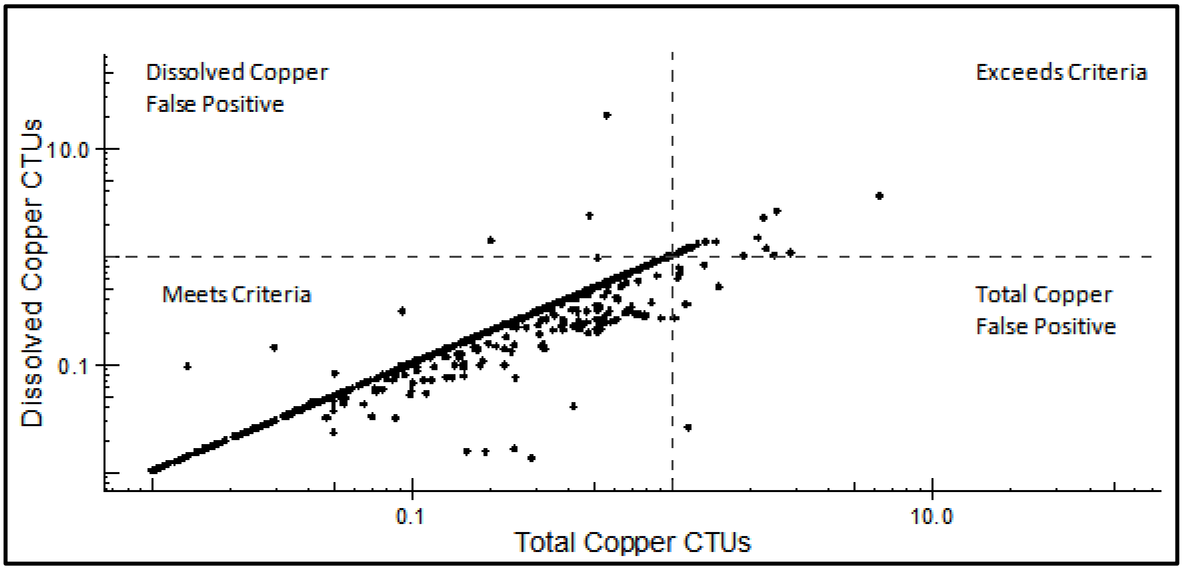


Table 40: Comparison of paired copper samples to IWQC and chronic toxic units

Comparison	Samples (n)
$Cu_d > Cu_t$	57
Cu_d > IWQC	22
Cu_t > IWQC	30
False Positives	3
Cu_T False Positives	11

There were 1,293 samples that had paired dissolved (Cu_d) or total (Cu_T) copper measurements. Total copper concentration was converted to dissolved concentration using a translator of 0.96. While not derived from empirical data, the 0.96 translator was developed by the EPA to convert the value of a criterion based on dissolved copper to a permit limit based on total recoverable copper.[68] There were 57 occurrences where $Cu_D > Cu_T$ (**Table 40**). This is likely due to sample variability, analytical error, or contamination in dissolved copper measurement, because dissolved Cu should not exceed total copper in the same sample. Despite the number of dissolved copper samples being higher than the concurrent measurements of total copper, 22 dissolved copper measurements exceeded the IWQC, while 30 total copper measurements exceeded the IWQC. Therefore, even though some dissolved copper samples may exhibit contamination, they do not appear to increase the number of times copper concentration exceeds the IWQC for a sample. Both the total and dissolved copper measures provided the same result of whether the copper was above or below the IWQC at a rate of 98.9%. Only 0.002% of dissolved copper samples indicated that the concentration was above the standard when total copper concentration was not, and only

[68] EPA 1996, The Metals Translator: Guidance for Calculating A Total Recoverable Permit Limit From a Dissolved Criterion. United States Environmental Protection Agency. EPA 823-B-96-007. June 1996.

0.008% of total copper samples indicated that the concentration was above the standard when dissolved copper was not.

In practice, dissolved copper concentrations should be used to assess compliance of a sample with BLM criteria. However, using existing total copper concentration data may be an alternative for assessing compliance with IWQC for samples where dissolved copper are not available. As a best practice, compliance programs should focus on collecting dissolved copper using methods designed to eliminate contamination and are sufficiently sensitive to achieve as low a detection limit as possible.

VIII.D Results Summary

- Dissolved Organic Carbon (DOC) and pH temporal trends at sites with long-term monitoring records:
    - Large, high-order rivers, such as the Columbia and Willamette Rivers, have relatively low DOC concentration (~2.0 mg/L) and appear relatively stable over time.
    - The tributary streams observed in the Willamette and Eastern physiographic regions showed a wider range of DOC concentration than high order streams.
    - pH values for large rivers and small tributaries for all the physiographic regions tend to have fluctuations in a relatively wide range of 1 pH unit. Streams in the Eastern region had significantly higher pH compared to streams in other regions of the state.
    - Hardness concentrations are less variable than DOC over time, indicating the BLM criteria may be expected to have greater time-variability than co-occurring hardness-based criteria.
    - Variability in parameter concentration was lower in large, high-order rivers relative to tributary streams.
- When comparing hardness-based criteria (HBC) to concurrent BLM criteria, approximately 52% of HBC were higher, and 48% of HBC were lower than the respective BLM criteria.
- Samples where the currently effective hardness-based criteria are higher than the BLM IWQC characteristically had significantly lower DOC (1.56 mg/L), pH (7.4) and sodium (5.75 mg/L) concentrations than sites where the hardness-based criteria were lower.
- DEQ may cautiously use total recoverable copper data when:
    - dissolved copper data are greater than total copper results, indicating potential sample contamination or some other data quality issue,
    - dissolved copper is not available, or
    - receiving water varies depending in part on the amount of suspended solids present.
- There were relatively few exceedances of BLM chronic IWQC for sites with available copper data. Copper concentration exceeded chronic IWQC in only 2% of samples statewide.
    - Sites with copper concentrations exceeding concurrent BLM IWQC were more likely to be observed in the Willamette Valley region.
    - The potential for exceeding criteria is potentially due to more frequent monitoring data, occasionally very dilute water chemistry conditions (low pH and TOC), and higher potential for anthropogenic sources of copper

IX. Model Applications

IX.A Objectives

The objective of this section is to evaluate the site-specific application of the Biotic Ligand Model to permitting and assessment. The specific objectives of this evaluation are to:

- Explore use of the Fixed Monitoring Benchmark (FMB) procedure to establish single acute or chronic criteria for developing water quality based effluent limits (WQBELs) for NPDES permits.
- Evaluate the number of site locations where sufficient data allow derivation of FMBs using long-term data records.
- Evaluate the number of samples, frequency of samples, and time span needed to capture critical temporal variation within sites, as needed, for applications such as the FMB analysis.

IX.B Evaluation of Site-Specific Criteria using Fixed Monitoring Benchmarks (FMBs)

The BLM IWQC determines a protective copper concentration that can be used to evaluate copper data for a specific sample time and location. Since water quality is affected by a number of factors, such as seasonal changes in productivity, precipitation amounts, and hydrologic sources, any water quality criterion development approach that relies on changing water quality characteristics will produce time-variable IWQC, including the BLM. The range of IWQC values that result from changes in water quality at some sites can be large (**Figure 46** and **Figure 48**), and this variation over time presents an additional challenge for regulators trying to determine a safe concentration.

To help address the complexity of time-variable IWQC, the FMB analysis may be used. The FMB is a probabilistic calculation included with BLM version 2.2.4 and later and can be used as a method to estimate a single protective copper concentration out of a time-variable water quality data set for a site. (see sections IV.D and VIII.B.2). The FMB extrapolates an observed frequency distribution to estimate a constant copper concentration that is defined such that in-stream dissolved copper concentrations at or below the FMB will not exceed the time-variable IWQC more frequently than a selected target exceedance frequency (e.g. 1 in 3 years).[69] Analyses of hundreds of BLM datasets show that the magnitude of the FMB is a function of the distribution of available IWQC at a site and the relative correlation between IWQC and copper concentration measurements[70]. The FMB can correspond to any percentile of the IWQC at a site, depending on how close copper concentrations are to their respective IWQC values, and the degree to which they are correlated. If copper concentration is consistently near the level of IWQC, the FMB will tend to be lower than the maximum copper concentration for the site,

[69] Santore, Robert C. (2015). *Overview of the Copper BLM*. Presentation at EPA BLM Workshop, Seattle, WA May 13-14, 2015.

[70] Ryan, Adam C. and Santore, Robert C. (2015). *Cu BLM, IWQC, and FMB. What are the tools for?* Presentation at EPA BLM Workshop, Seattle, WA May 13-14, 2015.

reflecting a higher probability that any given copper sample will exceed the IWQC given the distribution of copper data at the site.

IX.B.1 Evaluating Minimum Sample Sizes Required for Accurate FMB Determination

As the purpose of the FMB procedure is to capture the variability of BLM results over time, monitoring requirements for calculating FMBs are more extensive as it requires an adequate time series of coincident copper data along with BLM parameters for multiple IWQC calculations. Calculations for a reliable FMB assumes that:

> 1) Copper and IWQC data distributions fit assumptions of log-normality for the values of the toxic units relating copper concentration and IWQC.
>
> 2) Temporal variability in copper concentrations and BLM parameters have been adequately captured by the user's dataset.

DEQ received unpublished results of a series of statistical sub-sampling analyses by one of the primary developers of the BLM[71] who examined the ability of different sized sub-samples to approximate the true long-term geometric mean of IWQC for several rivers across the U.S. The analysis used a sub-sampling procedure to compare the effectiveness of various durations of simulated monitoring periods to capture the variability of data within a site. To conduct the analysis, the EPA STORET database was searched to identify locations that had a representative data set of BLM measurements that had been collected at approximately monthly intervals for five to six years.

As an example, DEQ presents the results from two rivers in the Pacific Northwest that were a part of that analysis: the Willamette River at Portland, OR (**Figure 60**) and the mouth of the Palouse River at Hooper, WA (**Figure 61**), which is a tributary of the Snake River. The Willamette River represents a large, high-order river with a relatively stable flow regime. The distribution of IWQC from the Willamette ranged from ~1.5 to ~10.0 µg/L Cu, with a geometric mean of ~4.7 µg. The Palouse River represents a smaller tributary from an arid, variable flow regime with more extremes in stream chemistry conditions. The distribution of IWQC from the Palouse ranged from <1 µg/L — >400 µg/L Cu, with a geometric mean of ~45 µg/L.

The distribution (top panels, red curves) and geometric mean (grey vertical lines) of IWQC from the entire data set at each location provided a representative sample with a geometric mean that was assumed to represent a long-term reference value for each site that could be used to assess the adequacy of any sub-sampling method. Monitoring datasets of various lengths were simulated by repeated sub-sampling of contiguous periods of one month, three months, six months, 12 months, and 24 months from the representative location (see legends, **Figure 60** and **Figure 61**). The distribution of the IWQC results for each sub-sampled dataset were compared to the reference value (see vertical grey lines, **Figure 60** and **Figure 61**). In each figure, the statistical distribution of estimates of the geometric mean IWQC for each

[71] Santore, Robert C. Personal Communication. Windward Environmental, LLC. Syracuse, NY. September 19, 2015.

sub-sampled dataset is shown as a probability density function, or “bell curve” (top panels) and as a percentile, or probability distribution, (bottom panels) of the population of IWQC values. Each of the simulated monitoring periods, from single months to 24 consecutive months, is shown in a different color (see legends). These curves show the distribution of estimates of the geometric mean IWQC that were calculated for repeating multiple sub-samplings of sets of IWQC for each of the simulated monitoring periods. A wide distribution indicates that the simulated monitoring period is not very accurate at estimating the true geometric mean of the population, as repeated sub-samplings provided a wide range of values that over or under-estimate the reference geometric mean. Narrow curves represent samples where estimates of the geometric mean were relatively consistent, and wider curves show samples where estimates of the geometric mean were highly variable. The peak of each curve can be compared to the geometric mean (grey vertical line) of the long-term representative sample.

The observed variability in estimated geometric means was relative to the number of samples. Monitoring datasets of three or six months duration were much more variable than those of 12 to 24 months compared to the geometric mean of the long-term reference dataset. In river systems such as the Palouse (**Figure 61**) where the actual distribution of IWQC were log-normally distributed and skewed right (**Figure 61**, top panel, red curve) monitoring regime periods of shorter duration (3-6 months) are more likely to overestimate the geometric mean and distribution of IWQC of the reference data set (**Figure 61**, bottom panel, blue line). Sampling periods of short duration are less accurate in estimating the population long-term geometric mean in general. The skew towards higher values in shorter monitoring periods indicates they are more likely to generate a higher estimate of the geometric mean.

Figure 60: Effect of sample size on estimates of IWQC for the Willamette River, OR (courtesy of Windward Environmental, LLC.)

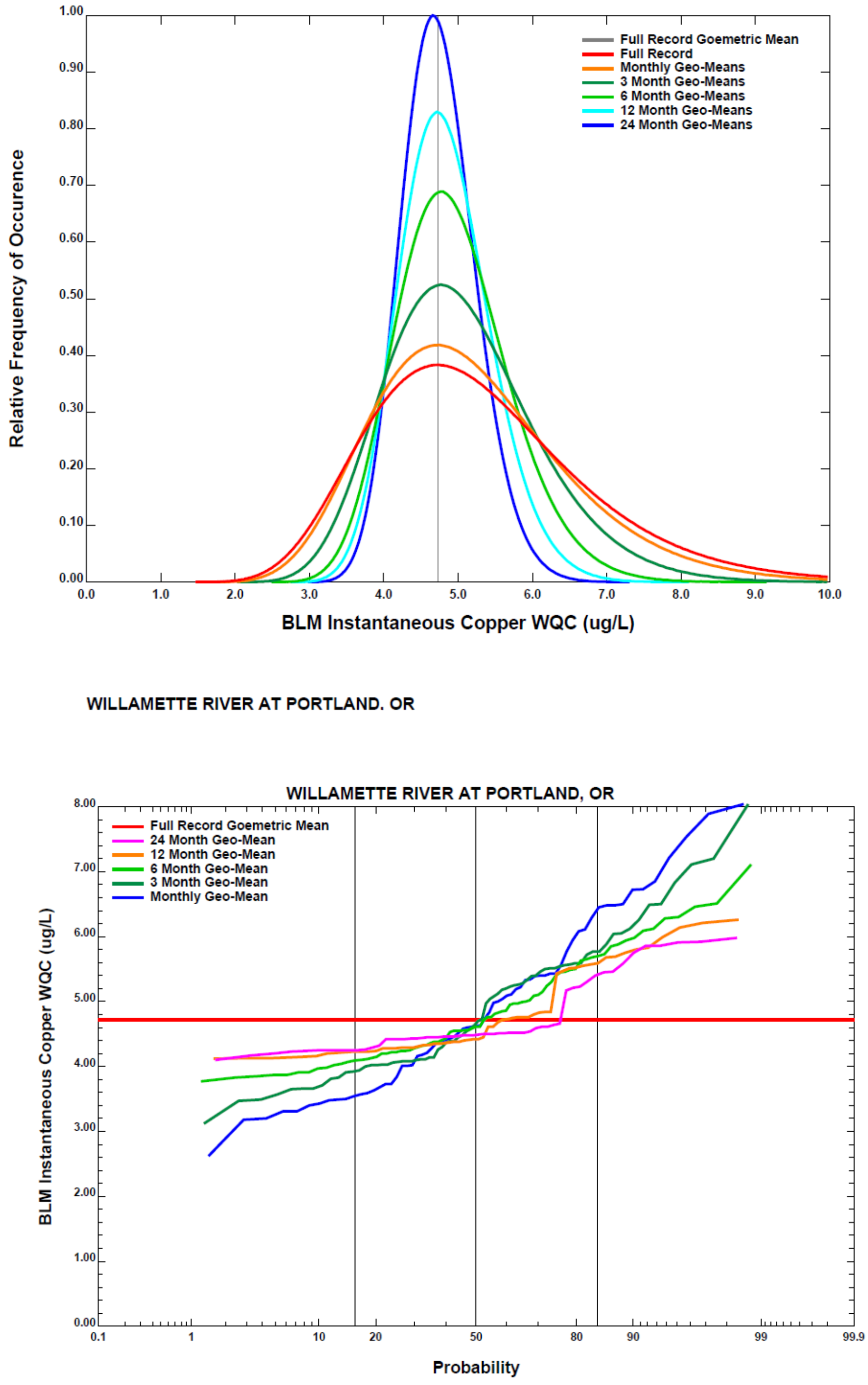
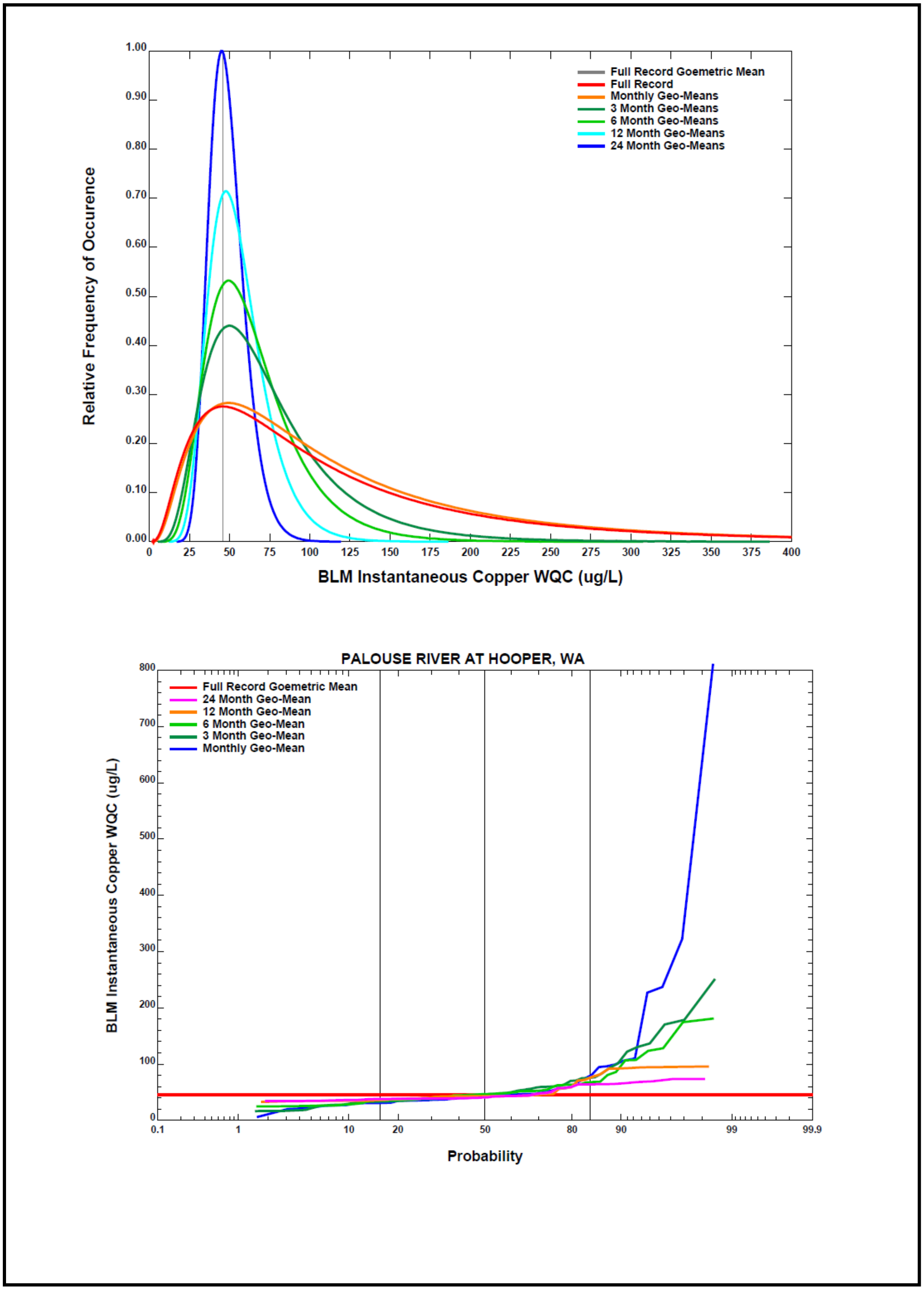


Figure 61: Effect of sample size on estimates of IWQC for the Palouse River, WA (courtesy of Windward Environmental, LLC.)



The analysis provided to DEQ examined the effect of sample size on providing accurate estimates of the geometric mean of IWQC for application to the FMB. However, the analysis may also support assumptions about the sample size needed to capture variation in parameter concentrations at sites where the resulting IWQC may vary significantly over time. Methods other than the FMB, such as those based on the EPA TSD for Toxics Control, may also be used to determine a protective criteria level where time-variability in BLM IWQC is observed. Although this analysis is relatively subjective, the data indicates that across a number of different river systems, monitoring periods of less than 12 monthly samples produces highly variable estimates of criteria, with potential bias that overestimates the geometric mean.

IX.B.2 Oregon Sites Suitable for FMB Determination

The User's Guide[72] for BLM version 2.2.4 states that fewer than nine monthly samples is not recommended for characterizing the environmental variability within a site and for use in calculation of a FMB criterion. The state of Colorado, which is adopting the FMB on a site-specific basis into their copper water quality standards in conjunction with developing NPDES permits, requires at least 24 samples spanning a minimum of 2 years[73].

In the Oregon BLM database, there are currently 91 sites that have the minimum of nine samples suggested in the BLM Manual, and 21 sites with 24 or more samples consistent with FMB guidelines provided by Colorado (**Table 41**). These sites have samples with at least data for DOC, pH, specific conductance, and dissolved or total copper data. These sites exist in all four physiographic regions of the state, but are concentrated in the Willamette Valley, where most sites are located, and most permitted copper discharges are expected to occur. Ongoing BLM monitoring by DEQ is anticipated to provide an additional 23 sites roughly equal across each region, with at least 12 additional samples of copper by Spring 2016.

[72] Hydroqual 2009. Biotic Ligand Model Windows Interface, Version 2.2.4. User's Guide and Reference Manual.

[73] Colorado Department of Public Health and Environment, 2015. Biotic Ligand Model Guidance Outline, Jan. 16, 2015.

Table 41: Oregon sites with minimum numbers of samples for FMB determination

	Number of sites (n)		
Region	**≥9 Samples**	**≥12 Samples**	**≥ 24 Samples**
Coastal	6	1	1
Willamette Valley	63	61	20
Cascades	5	4	0
Eastern	17	1	0
Total Sites	**91**	**67**	**21**

IX.C Results Summary

- At least 12 to 24 monthly samples may be necessary to accurately estimate the temporal variability of BLM IWQC at a site. Understanding this variability is important when setting permit limits through a "fixed monitoring benchmark" (FMB) procedure.
- Concurrent IWQC and dissolved copper data are needed to generate a FMB.
    - DEQ calculated FMBs for 67 sites in Oregon with 12 or more samples having sufficient BLM parameters and dissolved copper data available.
- Using a conservative percentile from the distribution of calculated IWQC may be sufficient as a surrogate for the FMB for waters where no copper data are available.

X. External Technical Review Panel: Summary of Responses and Conclusions

This section summarizes comments from the external technical review panel on some of the substantive analyses contained in the technical support document. DEQ did not attempt to summarize all comments or address all issues raised, but instead posed a number of overarching technical questions to the panel for their input. Not all reviewers responded to these questions. DEQ incorporated, as appropriate, a number of edits, analyses or suggestions throughout the document from panel members based on two separate review opportunities.

1. Is it valid to estimate BLM geochemical ion input parameters with measured conductivity data based on DEQ regression analyses?

DEQ found strong regression relationships derived from the Oregon dataset between geochemical ions and alkalinity values and measured conductivity data. Reviewers either supported the use of these statewide regression equations based on measured conductivity data to fill in missing geochemical ion data or did not express any concern. A reviewer noted that development of site-specific regression equations to estimate missing parameters should also be encouraged where possible.

Reviewers indicated that using conductivity measurements for missing geochemical ions could be a simplifying step for both prospective data collection and for filling data gaps retrospectively. In addition, the geochemical ion inputs are not as sensitive as other BLM inputs, such as DOC and pH, in driving protective copper criteria as demonstrated by an Oregon-specific sensitivity analysis. However, several reviewers also encouraged site-specific data collection of geochemical ions whenever possible, particularly where concentrations of specific ions are known or suspected to diverge from expected concentrations.

One reviewer had additional comments about conductivity data. For example, continuous conductivity data could help shed light on whether various temporal patterns might be significant in determining BLM outcomes, such as seasonal, periodic, or baseflow/stormflow discharges. Conductivity may also be used to estimate hardness (Ca and Mg ions) to evaluate similar impacts on hardness-based metals water quality criteria. The commenter further noted that DEQ should confirm use of specific conductance as conductivity data, which is temperature-adjusted, rather than raw conductivity data. DEQ confirmed that the data used in this analysis and will continue to use for estimating the ion inputs to the BLM is specific conductance.

Based on the poor correlation of DOC and pH with specific conductance and the high sensitivity of BLM outputs to these parameters, DEQ and the reviewers agreed that specific conductance should not be used to estimate DOC or pH.

2. Are DEQ's proposed methods to use total recoverable data for BLM parameters when dissolved data are absent reasonable?

DEQ's objective for analyzing total recoverable and dissolved BLM parameter relationships was to evaluate whether the magnitude of error introduced by using BLM input parameters based on total recoverable data, which comprises a significant portion of existing DEQ and USGS data, would influence criteria derivation results. DEQ would then use this information to evaluate whether the potential error was acceptable when applying the BLM. Overall, reviewers stressed that because the BLM is designed to use dissolved parameters, DEQ should require users to collect dissolved parameters for BLM purposes in the future, which would result in the most accurate criteria. Reviewers had specific input based on individual input parameters below:

- **Geochemical Ions and Alkalinity**
  Given the general strength of relationships between paired total recoverable and dissolved data, and the relative insensitivity of the model to changes in concentration of geochemical ions, the reviewers supported interchangeable use of total recoverable and dissolved data for the geochemical ions and alkalinity. Several reviewers suggested that best professional judgment be retained for situations where it is known or suspected that the total recoverable and dissolved measurements of parameters may diverge.

- **Copper**
  Copper data is not an input parameter in the BLM. However, dissolved copper data is required to use the Fixed Monitoring Benchmark approach or for assessment or compliance determinations. Most reviewers advised DEQ to use dissolved copper data at sufficiently low detection limits, rather than total recoverable data for applying the BLM because the relationship of total to dissolved metals, including copper, can vary under certain circumstances. For example, in conditions of high total suspended solids, the dissolved fraction of copper is typically much lower. The dissolved fraction can also vary in stormwater and wastewater effluent. One reviewer commented that the use of total recoverable data would greatly bias results under frequently observed instream conditions.

  When necessary, a reasonable translator for converting total recoverable to dissolved copper concentration would be appropriate where only total recoverable copper data exist. Most reviewers, however, agreed that the EPA-derived copper translator of 0.96[74] is overly conservative and would not be appropriate in many circumstances. One reviewer further stated that because of the uncertainty related to the EPA translator, DEQ should use a translator of one. Several reviewers recommended that DEQ require collection of paired dissolved and total metals data in order to develop reliable translators on a statewide or site-specific basis.

[74] EPA. Charles Stephan. 1995. Derivation of Conversion Factors for the Calculation of Dissolved Freshwater Aquatic Life Criteria for Metals. Environmental Research Laboratory—Duluth. Office of Research and Development.

The panel did not discuss risk implications associated with the conservative use of total recoverable copper data versus discarding total recoverable copper data when dissolved data are not available.

Most of Oregon's metals criteria are now expressed as dissolved, but this only recently occurred in 2013 following EPA approval of a number of aquatic life criteria for metals and other toxic pollutants. Therefore, much of the data collected in Oregon has been total recoverable data, which is still the form used for compliance with the human health metals criteria. DEQ's practice is to conservatively use total recoverable metals data for evaluating whether waterbodies are meeting the aquatic life metals dissolved criteria when dissolved metals data are absent. Several years ago, DEQ began collecting both total recoverable and dissolved metals data at approximately 178 locations throughout the state as part of DEQ's ambient and toxics monitoring network. As more dissolved data is collected throughout the state, DEQ will be able to use the most relevant data for impairment decisions related to the Integrated Report. DEQ will likely evaluate various methods to develop potential metals translators, including copper, in a more holistic manner as part of developing the assessment methodology for the Integrated Report. NPDES dischargers have the flexibility to collect both dissolved and total recoverable metals data to develop site-specific translators for permit development (See "Instructions for Dissolved Metals Criteria" at http://www.deq.state.or.us/wq/standards/toxics.htm).

- **Organic Carbon**

  Many organic carbon samples collected throughout Oregon are in the form of total organic carbon. Because the BLM accounts for metal bioavailability, dissolved organic carbon is a better metric for determining the amount of organic carbon available for binding with dissolved copper than TOC. DEQ's sensitivity analysis, and supported by other studies, show that DOC is a major driver in the BLM that accounts for copper bioavailability, and thus toxicity, in aquatic systems. Rather than discard TOC samples, DEQ conducted an analysis to assess whether a ratio of TOC to DOC could be developed in order to use existing TOC data. The statewide assessment showed that a translator of 0.83 was reasonably accurate.

  Several reviewers were comfortable with the use of this translator or did not express concern. Several others expressed concern about using one translator statewide, since there could be regional differences in TOC and DOC ratios. Also, because a large number of samples were collected in the Willamette Basin, using the translator statewide could bias the results for other locations. Using TOC data overestimates the availability of organic carbon to complex with dissolved copper, which could under-protect aquatic life. To evaluate this concern, DEQ conducted a non-parametric test on the distribution of DOC concentration in each of four physiographic regions of the state. DEQ found that each region of the state had a statistically different distribution of DOC concentration, with median DOC the highest in the Eastern region, followed by the Willamette Valley region. The median DOC concentration in each region was statistically different from the statewide median, and from the median within each other region. Development of a regional translator for TOC to DOC is likely a more accurate method than a statewide default given the data available in Oregon. However, there were not enough samples in the Cascade and Coastal regions to develop a statistically significant regression coefficient to use as a translator. Region specific conversions of TOC to DOC provide only a negligible incremental improvement in accuracy as a predictor for estimating missing DOC data from available TOC data. The statewide translator of 0.83 is reasonably accurate and provides the simplest available method.

To reiterate, the best method to develop BLM criteria is to collect DOC. However, in order to derive BLM criteria where TOC data are available and DOC data are not available, DEQ will use the best available translator.

3. Is DEQ's proposed methodology for developing new physiographic regions using specific conductance, pH and DOC, and potential estimates resulting from this delineation reasonable?

DEQ evaluated whether regions of the state could be delineated based on specific conductance (and by extension, geochemical ions), DOC and pH data. If so, in circumstances where BLM data are not available, DEQ or other users could estimate the missing parameter based on measured specific conductance, DOC or pH data in these regions, or estimate BLM criteria based on criteria developed at nearby sites with measured data in these regions. Most reviewers found that the method for identifying the four physiographic regions was reasonable, but were cautious about using estimates for pH, DOC or criteria based on physiographic averages or medians because the model is sensitive to these parameters and these parameters can vary widely within the four regions. Some suggested that any resulting estimated criteria should be viewed as screening values, rather than regulatory values. Reviewers' confidence was higher in developing site-specific estimates of DOC and pH when possible, or refinement of regional DOC and pH distributions based on underlying biogeochemical factors, such as geology. One reviewer suspected that seasonal variability in DOC will be more important than spatial variability. Another reviewer added that DOC seasonal variability may be particularly important in the coastal region. Also, diurnal variation in pH is a significant issue during the summer, so the time of day sampling is done could be more important than physical location in determining differences. DEQ stated that pH is a parameter commonly collected throughout Oregon and therefore, staff do not anticipate a great need to estimate this parameter.

Several reviewers noted that DEQ should lay out a clear approach for dischargers to use site-specific BLM data because it provides more reliable and accurate criteria than relying on regional estimated values.

4. In absence of DOC data, is it defensible to derive conservative estimates of DOC to use as BLM inputs following the methodologies presented by EPA and DEQ? Is either the EPA or DEQ method or data set more defensible than the other and if so, why?

Most reviewers agreed, or did not express concern, that the ideal approach is to collect the necessary DOC data in order to produce accurate model results given the sensitivity of this parameter in deriving BLM criteria. There was no consensus on the best method for estimating DOC values. One reviewer indicated that 10th percentile estimates of DOC might be used similar to calculating a 10th percentile hardness-based metals criteria for reasonable potential and wasteload allocations, albeit potentially over conservative. Another reviewer commented that the analysis should not only focus on what provides the most conservative outcome. Instead, the analysis should seek what most accurately predicts criteria in a given region, which provides a balance between false negatives and false positive outcomes from using conservative estimators. Several reviewers commented that what to do in the absence of data is ultimately a policy decision.

Reviewers discussed differences between the DEQ and EPA databases used to estimate DOC. The DEQ database captures a broader range of conditions over which the BLM model would be applied, while the EPA database better represents background DOC conditions and used a randomized sampling methodology. The DEQ database contains some non-randomly selected, disturbed or contaminated sites, with over-representation of data from the Willamette Valley. The EPA database represents small-order and wadeable streams, rather than valley-bottom streams and wastewater discharge receiving waters, where BLM parameters may be very different. Some reviewers expressed concern that selecting estimates based on a 10^{th} percentile DOC from the EPA database may be too conservative.

Several reviewers thought that DEQ's database is generally supportable for estimating DOC, as long as there is sufficient QA/QC and filtering of non-representative data. One reviewer noted that the question of whether DEQ's or EPA's database was more defensible depended on the application toward which it is applied.

5. For derivation of BLM criteria at sites with insufficient measured data, is it more defensible to: (1) estimate missing model input parameters or (2) apply estimated BLM criteria based on a specified protective level of the IWQC distribution from the associated physiographic region?

Most reviewers agreed that estimating BLM inputs for missing parameters was preferable to assigning estimated IWQC based on selecting a conservative value from a distribution of model outputs for a region and applying that value to all sites with insufficient measured data. Using input data that are available for a sample serves to reduce the uncertainty of the IWQC compared to applying a single conservative IWQC for a large area. Several reviewers further clarified that preference by stating that estimating geochemical ions or alkalinity from measured specific conductance data at specific locations would be more defensible than estimating pH, DOC or temperature. One reviewer added that estimating temperature or providing regional/seasonal reference values is defensible without further technical basis given its relative insensitivity in the BLM. Several reviewers cautioned that estimating too many parameters could lead to water chemistry that does not exist in the environment, as the relative ratio of ions is accounted for in the calculation of criteria. One reviewer said this document should stress that once sufficient data are collected, measured site-specific values for DOC and pH should take supremacy over estimated values as BLM inputs.

One reviewer provided a hierarchy of deriving BLM criteria for a specific site based on the level of measured data available for that site. Number one represents the most preferable, while number four represents the least preferable:

1) Collect and use the input parameter data needed to run the BLM model and calculate copper criteria over a range of conditions
2) Estimating missing model parameters using
    a. Site-specific regression analysis
    b. Broader geographic regression equations
3) Apply a default value(s) for estimating missing model parameters based on physiographic region

4) Apply a default IWQC value

A number of reviewers noted that determining which approach is more defensible also partly depends on how DEQ will apply the resulting criteria derived from estimated parameters. For example, using estimated values for sensitive BLM parameters, such as pH and DOC could be adequate for screening values, but perhaps is not sufficiently accurate to apply as regulatory criteria for NPDES permitting or for the Integrated Report. For example, if copper data exceed the screening value, then additional BLM data should be collected to verify exceedance of the copper standard. One reviewer added that requiring BLM users to collect some initial pH, DOC and specific conductance data is a very low cost and should be feasible for rapid initial screening. Another reviewer said this data could also ground-truth the available BLM database to examine how similar the data are for specific seasons to similar seasonal temporal ranges in the database.

6. Does DEQ have sufficient information to establish a minimum number of samples to be used for setting permit limits or for assessing waterbody impairment for the Integrated Report?

DEQ reviewed data collected by a consultant that used a sub-sampling procedure to compare the accuracy of various monitoring periods to represent the variability of data within a site at several rivers across the U.S. (i.e. how did the number of sampling events approximate the true geometric mean of BLM criteria?). From these data, DEQ determined that simulated monitoring datasets of less than 12 months in duration tended to be highly variable and did not accurately estimate the geometric mean of the long-term reference dataset. For this same dataset, another reviewer indicated that 9-12 samples provided good agreement with the real mean of the reference dataset. One reviewer thought that the minimum number of samples was more of a concern when applying the FMB to calculation of permit limits, and it was not a statistic that needed to be applied everywhere. Another reviewer recommended monthly monitoring for one year for permit development.

Several reviewers commented that the number of samples needed to capture temporal variability at a site is no different for copper than for any other water quality criterion. Guidance is available, such as the EPA TSD for toxics control for addressing limited data. Another reviewer recommended that DEQ look at a WERF 2007 report for ideas on minimum number of samples based on a state survey. Several reviewers suggested that DEQ should retain best professional judgment on a case-by-case basis regarding the adequacy of any particular data set. Other ideas included sampling specific or sensitive times of the year, or developing seasonal criteria to account for known variation in sensitive parameters, rather than establishing a blanket requirement for a specific number of samples at every site where criteria are developed.

7. Given the temporal variability of the BLM input parameters, and therefore of the IWQC at a site, the FMB method may be an option for developing protective effluent limits for copper. Are there scientifically credible alternatives to the FMB approach for setting permit limits that adequately represent the site, account for temporal variability and provide sufficient protection?

Most reviewers concurred that the FMB provides an effective method for evaluating coincident measures of ambient copper with the derived IWQC, and this approach could be effectively used for developing water quality based effluent limits. However, one reviewer recommended that this approach be postponed until there are a sufficient number of sites with sufficient samples across all DEQ physiographic regions to conduct a more complete Oregon BLM FMB analysis. Another reviewer indicated that the FMB is probably the best and most explicit option to account for site variability, although there are datasets and sites for which a FMB can either not be derived (e.g. insufficient or no copper data), the data don't fit the model very well, or the inherent assumptions such as log-normal distributions are not met. One reviewer suggested that since the FMB uses toxicity units, it could also be useful for determining assimilative capacity, or developing TMDLs.

One reviewer suggested that Oregon should explore how the FMB approach might be used appropriately for NPDES permits. EPA has not provided guidance in this regard, such as whether a FMB value can or should be used directly as an enforceable limit in NPDES permits or whether it is appropriate to use a FMB as an input to the reasonable potential analysis and waste load allocation calculations when following guidance in the EPA TSD for toxics control[75]. Colorado has begun the process of using FMBs in NPDES permits. Careful consideration will be warranted where FMBs may be significantly different upstream and downstream of a permitted discharge. A FMB developed for a sampling station downstream of a discharge is likely to represent variability in both the mixed ambient/effluent and criteria differently than as accounted for in a steady state mixing approach based on separate effluent and upstream water quality data. Another reviewer commented on deriving FMB values using downstream data. Although it is reasonable to use downstream water quality conditions, it might not make sense to use downstream water as the dilutant in mixing zone calculations if also using effluent data. It might be double counting the effect of effluent on water chemistry.

One reviewer described several alternatives to the FMB that are contained in the EPA TSD for toxics control, including log-normal probabilistic modeling (similar to the FMB), dynamic mechanistic models, which may be helpful if multiple sources exist, or Monte-Carlo modeling to account for variation. DEQ could also apply flow-based or seasonal limits where a more simple and straightforward approach is warranted. One commenter noted that the low flow condition, which permitting typically uses for permit limit development, is not necessarily the worst-case scenario for determining compliance with BLM copper criteria.

Several commenters suggested that if the FMB cannot be used then the IWQC percentile approach may be retained as an option, but with the understanding that the appropriate percentile may be highly variable between sites and should be considered carefully. Several commenters suggested that a percentile approach seems best as a screening level and not as a regulatory number for permit compliance or assessments. Regardless, exceedances of limits established using the FMB or IWQC percentile should be verified against concurrent IWQC values.

One reviewer stressed that DEQ should allow for best professional judgment for developing protective effluent limits because the process of adopting protective state criteria is different than the methods used to implement the criteria.

8. Given the temporal variability of the BLM, what are the scientifically credible options for evaluating copper data for 303(d) assessment purposes? One option is to evaluate each copper data point with the BLM IWQC derived for the same sample event. Another option may

[75] EPA. Technical Support Document for Water-quality Based Toxics Control. EPA/505/2-90-001. PB91-127415. March 1991.

be to establish a protective BLM IWQC based on the distribution of IWQC (for example, 10th percentile or median IWQC) for a site over time and compare that IWQC to copper data.

Overall, some reviewers believed that 303(d) listing was not adequately considered in the document, however, several reviewers provided ideas about how to evaluate copper data for 303(d) assessment purposes.

Several reviewers thought the FMB approach would be useful for assessing compliance for the Integrated Report and would be the scientifically credible approach.

One reviewer suggested modifying the existing approach DEQ uses for hardness-based criteria, and apply the same general approach to BLM criteria. For example, compare a fixed percentage of ambient copper concentrations, such as the 85th percentile, with a fixed percentage IWQC value for a stream segment, as long as there is a representative dataset for deriving the IWQC percentile. Another commenter indicated that an arbitrary percentile based on IWQC carries an error rate that may be unacceptable, but could be used for initial screening. TMDLs and 303(d) listing decisions should be based on good quality data with a high degree of certainty in addressing real problems given the impact and costs associated with waterbody impairment designations.

Another reviewer suggested that the IWQC are the most accurate compliance decision tool in terms of criteria magnitudes. For example, DEQ could use paired copper and IWQC to determine listings for 303(d) assessment. One commenter indicated that there could be value in establishing a conservative percentile prior to assessment for temporally and spatially appropriate IWQC, particularly where there are no copper discharges. Attaining the criteria at a low percentile provides confidence that waters are protected. Another reviewer suggested that DEQ should provide input to the advisory committee on alternative listing strategies for 303(d) assessment purposes, such as data needed for impairment decisions, when more data are needed, or what data would support attaining the copper standard.

9. Compounded conservatism of BLM inputs and criteria application

One reviewer had several concerns with the “compounded conservatism” associated with using 10th percentile BLM default values when measured values are not available, particularly when used for both pH and DOC. The reviewer asked DEQ to provide additional plots comparing measured IWQC to IWQC developed using various percentiles, such as 10th, 25th, median and 75th percentile, of DOC and pH. Ultimately, the amount of conservatism embodied in the final copper criteria is a policy decision, but some estimate of the amount of conservatism each percentile choice results in, such as the percent of calculations where the estimated IWQC exceeds the measured IWQC would be helpful to policy makers. Another means of illustrating the amount of conservatism resulting from use of various defaults (10th percentiles or otherwise) for DOC and pH is to reproduce **Table 38** in the TSD for the four DEQ physiographic regions using various default levels for DOC and pH. The number of exceedances and exceedance percentage (column 3 and 4 in **Table 38**) using the various defaults will provide policy makers an indication of the conservatism inherent in the final criteria.

Several other reviewers indicated that by picking very conservative pH and DOC values when measured values are absent can result in water chemistry that does not occur in the environment, revisiting this argument initially described above under number five. The exception would be in those circumstances where both very low pH and DOC concentrations truly co-occur in the environment.

10. Multiple linear regression approach to derive copper criteria

One reviewer recommended that DEQ develop an alternative multiple linear regression (MLR) approach using the BLM framework. The alternative equation would be more similar in form and application to the current hardness-based equations for metals:

Example: $BLM_{CCC\ or\ CMC}$ = f(DOC, pH, Temperature, Conductivity)

Another reviewer commented that there are different kinds of MLR approaches available, and that different approaches could have different policy implications. For example, one approach is to generate a MLR equation that correlates BLM IWQC values to distributions of pH, DOC, or other parameters for a particular area or dataset. This approach may be less subject to additional EPA review and ESA consultation because the underlying BLM IWQC calculation still forms the basis of the criterion.

The review panel briefly discussed recent work by several researchers (Kevin Brix and David DeForest) who have developed another kind of MLR model for copper based on three important BLM parameters—DOC, hardness and pH—to derive protective copper criteria. Several advantages to this method include a reduction in the number of input parameters needed, and ease of determining criteria through the development of look-up tables based on ranges of the three input parameters. Although several of the reviewers view this work as promising, the panel acknowledged that there needs to be a better understanding of where the BLM results diverge from MLR-derived criteria. This work has yet to be reviewed and published. In addition, this model would need EPA review and likely ESA consultation depending on the differences between BLM-derived and MLR-derived criteria. DEQ and several panel members agreed that it would be difficult for DEQ to pursue this methodology in a timely manner given the current state of development and some of the unknowns associated with this derivation method.

Appendix A:

List of USGS and DEQ water quality monitoring sites (n=164) with samples containing a complete set of all measured BLM parameters.

Site ID	Description	Latitude	Longitude	Data Source	EPA Level-III Ecoregion	HUC 4 Watershed	Oregon Physiographic Region	Number of samples (n=361)
10332	Willamette River at SP&S RR Bridge (Portland)	45.57795	-122.7475	DEQ-BLM Monitoring	Willamette Valley	Willamette	Willamette Valley	2
10339	Willamette River at Canby Ferry	45.29984	-122.692151	DEQ-BLM Monitoring	Willamette Valley	Willamette	Willamette Valley	1
10344	Willamette River at Wheatland Ferry	45.090209	-123.045407	DEQ-BLM Monitoring	Willamette Valley	Willamette	Willamette Valley	1
10350	Willamette River at Albany (eastbound Hwy 20 bridge)	44.639008	-123.105146	DEQ-BLM Monitoring	Willamette Valley	Willamette	Willamette Valley	1
10352	Willamette River at Old Hwy 34 Bridge (Corvallis)	44.565249	-123.256693	DEQ-BLM Monitoring	Willamette Valley	Willamette	Willamette Valley	1
10391	Siletz R 5 miles DS of Siletz at RM 29.9	44.764267	-123.915022	DEQ-BLM Monitoring	Coast Range	Oregon-Washington Coastal	Coastal	4
10406	Umatilla River at Hwy 11 (Pendleton)	45.674526	-118.759654	DEQ-BLM Monitoring	Columbia Plateau	Middle Columbia	Eastern	2
10407	Malheur River at Hwy 201 (Ontario)	44.0532	-116.981582	DEQ-BLM Monitoring	Snake River Plain	Middle Snake	Eastern	2
10410	Wallowa River at Minam	45.620792	-117.719692	DEQ-BLM Monitoring	Blue Mountains	Lower Snake	Eastern	2
10411	Deschutes River at Deschutes River Park	45.632493	-120.912617	DEQ-BLM Monitoring	Columbia Plateau	Middle Columbia	Eastern	1
10414	Rogue River at Lobster Creek Bridge	42.5035	-124.293224	DEQ-BLM Monitoring	Coast Range	Oregon-Washington Coastal	Coastal	2

Site ID	Description	Latitude	Longitude	Data Source	EPA Level-III Ecoregion	HUC 4 Watershed	Oregon Physiographic Region	Number of samples (n=361)
10421	Rogue River at Hwy 234 (north of Gold Hill)	42.432239	-123.09071	DEQ-BLM Monitoring	Klamath Mountains	Oregon-Washington Coastal	Coastal	1
10423	Rogue River at Hwy 234 (Dodge Park)	42.524934	-122.842713	DEQ-BLM Monitoring	Klamath Mountains	Oregon-Washington Coastal	Coastal	1
10428	Applegate River at Hwy 199 (near Wilderville)	42.397381	-123.456994	DEQ-BLM Monitoring	Klamath Mountains	Oregon-Washington Coastal	Coastal	2
10443	South Umpqua at Hwy 42 (Winston)	43.133918	-123.399244	DEQ-BLM Monitoring	Klamath Mountains	Oregon-Washington Coastal	Coastal	2
10458	Tualatin River near Elsner Road	45.388341	-122.851459	DEQ-BLM Monitoring	Willamette Valley	Willamette	Willamette Valley	2
10461	Tualatin River at Rood Road	45.489959	-122.951495	DEQ-BLM Monitoring	Willamette Valley	Willamette	Willamette Valley	2
10480	Beaverton Creek at Cornelius Pass Road	45.520867	-122.900019	DEQ-BLM Monitoring	Willamette Valley	Willamette	Willamette Valley	2
10506	Deschutes River at Hwy 26 (Warm Springs)	44.76138	-121.228612	DEQ-BLM Monitoring	Blue Mountains	Middle Columbia	Eastern	2
10511	Deschutes River at Mirror Pond (Drake Park-Bend)	44.060348	-121.320907	DEQ-BLM Monitoring	Eastern Cascades Slopes and Foothills	Middle Columbia	Eastern	2
10521	Necanicum R at Forest Lake RV Camp (Seaside)	45.952055	-123.925061	DEQ-BLM Monitoring	Coast Range	Oregon-Washington Coastal	Coastal	4
10523	Nestucca R at Cloverdale	45.207035	-123.889895	DEQ-BLM Monitoring	Coast Range	Oregon-Washington Coastal	Coastal	2

Site ID	Description	Latitude	Longitude	Data Source	EPA Level-III Ecoregion	HUC 4 Watershed	Oregon Physiographic Region	Number of samples (n=361)
10555	Willamette River at Marion Street (Salem)	44.944392	-123.046256	DEQ-BLM Monitoring	Willamette Valley	Willamette	Willamette Valley	1
10582	Schooner Creek at Highway 101 Bridge (Lincoln City)	44.92675	-124.012583	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
10596	Coquille River at Sturdivant Park Dock (Coquille)	43.174516	-124.199353	DEQ-BLM Monitoring	Coast Range	Oregon-Washington Coastal	Coastal	2
10602	Little Butte Creek at Agate Road (White City)	42.455133	-122.856316	DEQ-BLM Monitoring	Klamath Mountains	Oregon-Washington Coastal	Coastal	1
10611	Willamette River at Hawthorne Bridge	45.51331	-122.66989	DEQ-BLM Monitoring	Willamette Valley	Willamette	Willamette Valley	2
10616	Columbia River at Marker #47 (upstream of Willamette River)	45.64564	-122.73886	DEQ-BLM Monitoring	Willamette Valley	Lower Columbia	Willamette Valley	2
10640	Pudding River at Hwy 211 (Woodburn)	45.150479	-122.792891	DEQ-BLM Monitoring	Willamette Valley	Willamette	Willamette Valley	2
10674	Sandy River at Troutdale Bridge	45.538462	-122.376913	DEQ-BLM Monitoring	Willamette Valley	Lower Columbia	Willamette Valley	2
10696	Little Deschutes River at HWY 42 (Road 2114)	43.820521	-121.451219	DEQ-BLM Monitoring	Eastern Cascades Slopes and Foothills	Middle Columbia	Eastern	2
10720	Grande Ronde River at Hilgard Park	45.341797	-118.236466	DEQ-BLM Monitoring	Blue Mountains	Lower Snake	Eastern	2
10730	Owyhee River at Rome (Hwy.95)	42.8407	-117.6228	DEQ-BLM Monitoring	Northern Basin and Range	Middle Snake	Eastern	2

Site ID	Description	Latitude	Longitude	Data Source	EPA Level-III Ecoregion	HUC 4 Watershed	Oregon Physiographic Region	Number of samples (n=361)
10765	Klamath River at Hwy 66 (Keno)	42.127618	-121.928353	DEQ-BLM Monitoring	Eastern Cascades Slopes and Foothills	Klamath-Northern California Co	Eastern	1
10768	Link River at mouth (Klamath Falls)	42.218429	-121.788966	DEQ-BLM Monitoring	Eastern Cascades Slopes and Foothills	Klamath-Northern California Co	Eastern	2
10770	Williamson River at Williamson River Store	42.51405	-121.916961	DEQ-BLM Monitoring	Eastern Cascades Slopes and Foothills	Klamath-Northern California Co	Eastern	2
10812	Skipanon River at Hwy 101	46.138517	-123.924282	DEQ-BLM Monitoring	Coast Range	Lower Columbia	Coastal	4
10948	South Yamhill River at Hwy 99W (Mcminnville)	45.168535	-123.207794	DEQ-BLM Monitoring	Willamette Valley	Willamette	Willamette Valley	2
10990	Wolf Creek at mouth	43.954889	-123.6205	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
10996	Calapooya Creek at Umpqua	43.366598	-123.46082	DEQ-BLM Monitoring	Klamath Mountains	Oregon-Washington Coastal	Coastal	2
10997	Cow Creek at mouth	42.942948	-123.336877	DEQ-BLM Monitoring	Klamath Mountains	Oregon-Washington Coastal	Coastal	2
11003	Three Rivers at Hebo Bridge	45.2299004	-123.860901	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1

Site ID	Description	Latitude	Longitude	Data Source	EPA Level-III Ecoregion	HUC 4 Watershed	Oregon Physiographic Region	Number of samples (n=361)
11005	Beaver Creek at Beaver	45.277444	-123.825667	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
11017	North Fork John Day River at Kimberly	44.756173	-119.638515	DEQ-BLM Monitoring	Blue Mountains	Middle Columbia	Eastern	2
11047	Malheur River at Hwy 20 (Drewsey)	43.785429	-118.331779	DEQ-BLM Monitoring	Northern Basin and Range	Middle Snake	Eastern	2
11051	Bear Creek at Kirtland Road (Central Point)	42.426867	-122.957354	DEQ-BLM Monitoring	Klamath Mountains	Oregon-Washington Coastal	Coastal	1
11201	Columbia Slough at Landfill Road	45.610638	-122.754711	DEQ-BLM Monitoring	Willamette Valley	Willamette	Willamette Valley	2
11229	Ecola CR at Cannon Beach Loop RD	45.90225	-123.958444	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
11241	Salmon River at Old Scenic Hwy 101 (Otis)	45.023127	-123.946701	DEQ-BLM Monitoring	Coast Range	Oregon-Washington Coastal	Coastal	1
11263	Alsea River at Thissell Road (Mike Bauer Park)	44.386272	-123.831288	DEQ-BLM Monitoring	Coast Range	Oregon-Washington Coastal	Coastal	3
11321	Johnson Creek at SE 17th Avenue (Portland)	45.446708	-122.643153	DEQ-BLM Monitoring	Willamette Valley	Willamette	Willamette Valley	2
11434	Clatskanie River at Hwy 30 (Clatskanie)	46.102027	-123.199456	DEQ-BLM Monitoring	Coast Range	Lower Columbia	Coastal	1
11476	Yaquina River at Trapp Road (Chitwood)	44.657546	-123.838911	DEQ-BLM Monitoring	Coast Range	Oregon-Washington Coastal	Coastal	4
11477	Crooked River at Conant Basin Road	44.172409	-120.54218	DEQ-BLM Monitoring	Blue Mountains	Middle Columbia	Eastern	2

Site ID	Description	Latitude	Longitude	Data Source	EPA Level-III Ecoregion	HUC 4 Watershed	Oregon Physiographic Region	Number of samples (n=361)
11479	John Day River upstream of Dayville	44.466	-119.47144	DEQ-BLM Monitoring	Blue Mountains	Middle Columbia	Eastern	2
11482	Illinois River downstream of Kerby	42.245705	-123.689155	DEQ-BLM Monitoring	Klamath Mountains	Oregon-Washington Coastal	Coastal	2
11484	South Umpqua at Days Creek Cutoff Road (Canyonville)	42.971243	-123.213878	DEQ-BLM Monitoring	Klamath Mountains	Oregon-Washington Coastal	Coastal	2
11489	Umatilla River at Westland Road (Hermiston)	45.835612	-119.332935	DEQ-BLM Monitoring	Columbia Plateau	Middle Columbia	Eastern	2
11490	Powder River at Hwy 7 (in Baker City)	44.78178	-117.82763	DEQ-BLM Monitoring	Blue Mountains	Middle Snake	Eastern	2
11522	South Umpqua at Stewart Park Road (Roseburg)	43.217407	-123.366509	DEQ-BLM Monitoring	Klamath Mountains	Oregon-Washington Coastal	Coastal	2
11571	North Fork Coquille River at Cooper Bridge	43.071667	-124.105972	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
11849	Salmonberry River at mouth	45.750361	-123.651778	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
11856	Nehalem River at Foley Road (Roy Creek Campground)	45.69983	-123.844162	DEQ-BLM Monitoring	Coast Range	Oregon-Washington Coastal	Coastal	1
12012	Hood River at footbridge downstream of I-84	45.710942	-121.50806	DEQ-BLM Monitoring	Eastern Cascades Slopes and Foothills	Middle Columbia	Eastern	2

Site ID	Description	Latitude	Longitude	Data Source	EPA Level-III Ecoregion	HUC 4 Watershed	Oregon Physiographic Region	Number of samples (n=361)
12187	Youngs River at Youngs River Loop Road	46.069889	-123.785604	DEQ-BLM Monitoring	Coast Range	Lower Columbia	Coastal	3
12189	Umatilla River upstream of McKay Creek	45.6716003	-118.833298	LASAR	Columbia Plateau	Middle Columbia	Eastern	1
12265	Donner Und Blitzen River upstream of Page Springs Campground	42.80108	-118.86658	DEQ-BLM Monitoring	Northern Basin and Range	Oregon Closed Basins	Eastern	2
12607	Tenmile Creek at Lakeside Marina (off Park Street)	43.573333	-124.175861	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
12951	Wilson River at Hwy 6 (Lee's Camp)	45.590194	-123.534889	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	1
12962	South Fork Trask River downstream of Edwards Creek	45.41575	-123.603972	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
13070	Clackamas River at Mciver Park (upper boat ramp)	45.29939	-122.36033	DEQ-BLM Monitoring	Willamette Valley	Willamette	Willamette Valley	2
13074	South Fork Big Butte Creek 50 feet upstream of WWTP outfall	42.547699	-122.567299	LASAR	Cascades	Oregon-Washington Coastal	Cascades	1
13411	Miami River at Moss Creek Road	45.574829	-123.873859	DEQ-BLM Monitoring	Coast Range	Oregon-Washington Coastal	Coastal	2
13424	Wilson R at HWY 6 at LLID RM 10.2	45.471854	-123.736706	DEQ-BLM Monitoring	Coast Range	Oregon-Washington Coastal	Coastal	1

Site ID	Description	Latitude	Longitude	Data Source	EPA Level-III Ecoregion	HUC 4 Watershed	Oregon Physiographic Region	Number of samples (n=361)
13431	Trask River at Netarts Road (Hwy. 6)	45.456389	-123.85853	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
13433	Trask River at Hwy 101	45.42944	-123.82389	DEQ-BLM Monitoring	Coast Range	Oregon-Washington Coastal	Coastal	2
13440	Tillamook River at Bewley Creek Road	45.407983	-123.824659	DEQ-BLM Monitoring	Coast Range	Oregon-Washington Coastal	Coastal	3
13569	West Fork Millicoma River at Allegany	43.425	-124.030556	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
14247	Bandon Landfill Ss-1 tributary of Seven Mile Creek	43.2024994	-124.356102	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1
14248	Bandon Landfill Ss-2 downstream of landfill	43.2089005	-124.3508	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1
14268	SS-2	43.2103005	-124.316399	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1
14434	Soap Creek upstream of Coffin Butte Landfill	44.6977997	-123.2444	LASAR	Willamette Valley	Willamette	Willamette Valley	1
14435	Soap Creek downstream of Coffin Butte Landfill	44.6994019	-123.246101	LASAR	Willamette Valley	Willamette	Willamette Valley	1
15009	SS-4	43.3167	-124.292198	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1

Site ID	Description	Latitude	Longitude	Data Source	EPA Level-III Ecoregion	HUC 4 Watershed	Oregon Physiographic Region	Number of samples (n=361)
15011	SS-2 Shana Creek upstream of Joe Ney Landfill north of SS-5	43.3213997	-124.298103	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1
15013	SS-5	43.3191986	-124.295799	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1
15577	Reedsport Landfill, Scholfield Creek upstream from landfill (SP#6)	43.6883011	-124.07	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1
15578	Reedsport Landfill, creek near B-4 (SP#7)	43.6906014	-124.071404	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1
15697	SW-3, Creek Below Roseburg Landfill	43.1847	-123.377197	LASAR	Klamath Mountains	Oregon-Washington Coastal	Coastal	1
15700	SW-1, Creek upstream of Roseburg Landfill	43.1851006	-123.387604	LASAR	Klamath Mountains	Oregon-Washington Coastal	Coastal	1
15785	Short Mountain Landfill upstream on Camas Swale Creek CS-1	43.9543991	-123.012199	LASAR	Willamette Valley	Willamette	Willamette Valley	2
15972	SW-1, creek at Sutland Road, south of Tillamook Landfill	45.4089012	-123.839996	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1
18802	North Fork Nehalem River at Highway 53	45.813472	-123.769111	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2

Site ID	Description	Latitude	Longitude	Data Source	EPA Level-III Ecoregion	HUC 4 Watershed	Oregon Physiographic Region	Number of samples (n=361)
20394	South Fork Coquille 50 feet upstream of Powers STP	42.8880997	-124.067398	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1
20434	Lake Creek at Deaddog Hole	44.070833	-123.788056	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
22394	Nestucca River at first bridge ramp (upstream of Beaver)	45.2765	-123.818167	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
23176	Woodburn Landfill SC-3	45.1817017	-122.860001	LASAR	Willamette Valley	Willamette	Willamette Valley	2
23199	Fox Hill Landfill SW-1 (upgradient of landfill, in Haywire Creek)	45.348999	-118.121399	LASAR	Blue Mountains	Lower Snake	Eastern	1
23200	Fox Hill Landfill SW-2 (downgradient of landfill, in Haywire Creek)	45.3469009	-118.122002	LASAR	Blue Mountains	Lower Snake	Eastern	1
23266	DRJ Landfill: Pond below woodwaste fill area	42.9618988	-123.363098	LASAR	Klamath Mountains	Oregon-Washington Coastal	Coastal	2
24299	Nehalem River at Hwy 47 Bridge upstream of Vernonia (River Mile 92.1)	45.843657	-123.201595	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
25754	South Fork Coquille River, River Mile 1.0, Myrtle Point boat ramp	43.066765	-124.147438	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
28303	Elk Creek at ODFW Hatchery	42.73667	-124.39916	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2

Site ID	Description	Latitude	Longitude	Data Source	EPA Level-III Ecoregion	HUC 4 Watershed	Oregon Physiographic Region	Number of samples (n=361)
28803	Ferry Creek downstream of ODFW Hatchery	43.1149	-124.3845	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
29900	Cummins Creek	44.267303	-124.09786	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
30670	Chetco River below Jack Creek	42.06427	-124.22897	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
31934	Crooked River 50 feet upstream of Prineville WWTP outfall	44.3132019	-120.872597	LASAR	Blue Mountains	Middle Columbia	Eastern	2
32060	Mill Creek upstream of Hubbard STP (Pudding River)	45.1860008	-122.813904	LASAR	Willamette Valley	Willamette	Willamette Valley	1
32446	North Fork Deep Creek upstream of Boring STP outfall at weir	45.426899	-122.377098	LASAR	Willamette Valley	Willamette	Willamette Valley	1
32497	South Santiam River 100 meters upstream of Sweet Home STP outfall	44.401001	-122.732597	LASAR	Willamette Valley	Willamette	Willamette Valley	1
32500	South Santiam River 100 feet downstream of Sweet Home STP outfall (mixing zone edge)	44.401001	-122.737999	LASAR	Willamette Valley	Willamette	Willamette Valley	1
32513	Mill Creek 100 feet downstream of Hubbard STP outfall (edge of mixing zone)	45.1864014	-122.813004	LASAR	Willamette Valley	Willamette	Willamette Valley	1

Site ID	Description	Latitude	Longitude	Data Source	EPA Level-III Ecoregion	HUC 4 Watershed	Oregon Physiographic Region	Number of samples (n=361)
32540	100 yards downstream of Hebo outfall	45.2304001	-123.062302	LASAR	Willamette Valley	Willamette	Willamette Valley	1
32541	Boquist Slough upstream of Pacific Campground outfall	45.4864006	-123.848198	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1
32794	Umatilla River upstream of Dillon Diversion Dam (upstream of Echo outfall)	45.7580986	-119.215599	LASAR	Columbia Plateau	Middle Columbia	Eastern	1
32871	Calapooia River, 80 feet upstream of Brownsville WWTP outfall	44.3951988	-122.998497	LASAR	Willamette Valley	Willamette	Willamette Valley	1
32878	Neskowin Creek 75 meters upstream of Neskowin WWTP discharge pipe	45.096199	-123.978401	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1
32880	Neskowin Creek 50 feet downstream of Neskowin WWTP outfall	45.0965996	-123.979202	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1
32980	Humbug Creek near mouth (Nehalem)	45.851162	-123.58465	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
33165	Boise Cascade Clarifier Solids, B2, upstream of fill area	45.8511009	-122.886398	LASAR	Coast Range	Willamette	Coastal	1
33642	Siuslaw River at Tide boat ramp	44.042712	-123.875851	DEQ-BLM Monitoring	Coast Range	Oregon-Washington Coastal	Coastal	4

Site ID	Description	Latitude	Longitude	Data Source	EPA Level-III Ecoregion	HUC 4 Watershed	Oregon Physiographic Region	Number of samples (n=361)
33929	Silvies River at West Loop Road	43.6341	-119.0771	DEQ-BLM Monitoring	Northern Basin and Range	Oregon Closed Basins	Eastern	2
34019	Nehalem River at Hwy 202 Bridge in Birkenfeld river mile 64.9	45.988833	-123.338694	DEQ-BLM Monitoring	Coast Range	Oregon-Washington Coastal	Coastal	2
34020	Applegate River, 50 feet upstream of Hidden Valley HS outfall	42.3437004	-123.332802	LASAR	Klamath Mountains	Oregon-Washington Coastal	Coastal	1
34032	Crooked River, 150 feet downstream of Prineville WWTP outfall	44.3088989	-120.868301	LASAR	Blue Mountains	Middle Columbia	Eastern	2
34115	Panther Creek at North Bank Road (Salmon River)	45.0087	-123.9151	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
34165	Clatskanie River above Fall Creek at Beaver boat ramp (Columbia)	46.1075	-123.206417	DEQ Toxics	Coast Range	Lower Columbia	Coastal	2
34425	Yachats River at RM 0.9	44.3091	-124.0938	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
34462	Sijota Creek, 140 ft u/s of Salishan WWTP outfall	44.8903008	-124.025597	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1
34478	South Fork Coquille 50 feet upstream of Myrtle Point WWTP outfall	43.0695	-124.1483	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1

Site ID	Description	Latitude	Longitude	Data Source	EPA Level-III Ecoregion	HUC 4 Watershed	Oregon Physiographic Region	Number of samples (n=361)
34481	South Fork Coquille 150 feet downstream of Myrtle Point WWTP outfall	43.0699005	-124.148399	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1
34489	Q Street Canal, 75 feet u/s of Dynea outfall	44.0536003	-122.985603	LASAR	Willamette Valley	Willamette	Willamette Valley	1
34491	Q Street Canal, 50 feet u/s of Pierce Channel mouth	44.0615006	-122.996399	LASAR	Willamette Valley	Willamette	Willamette Valley	1
34492	Q Street Canal, mouth of Pierce Channel	44.0615006	-122.996597	LASAR	Willamette Valley	Willamette	Willamette Valley	1
34494	Q Street Canal, 200 feet d/s of Pierce Channel mouth	44.0611	-122.997597	LASAR	Willamette Valley	Willamette	Willamette Valley	1
34496	Q Street Canal, 10 feet u/s of fish barrier	44.0625992	-123.041	LASAR	Willamette Valley	Willamette	Willamette Valley	1
34498	Q Street Canal, mouth of Canoe Channel	44.0584984	-123.076897	LASAR	Willamette Valley	Willamette	Willamette Valley	1
34499	Q Street Canal, Alton Baker Parkway spillway near Willamette River	44.0569	-123.082901	LASAR	Willamette Valley	Willamette	Willamette Valley	1
34539	Willamette River, 1 mile u/s of Tualatin mouth	45.3233986	-122.660797	LASAR	Willamette Valley	Willamette	Willamette Valley	1
34540	Tualatin River at mouth, 200 feet d/s of bridge	45.338501	-122.652802	LASAR	Willamette Valley	Willamette	Willamette Valley	1
34541	Willamette River, 300 feet u/s of I-205 bridge, right bank	45.3596001	-122.607803	LASAR	Willamette Valley	Willamette	Willamette Valley	1

Site ID	Description	Latitude	Longitude	Data Source	EPA Level-III Ecoregion	HUC 4 Watershed	Oregon Physiographic Region	Number of samples (n=361)
34542	Willamette River, 300 feet u/s of I-205 bridge, left bank	45.361599	-122.607597	LASAR	Willamette Valley	Willamette	Willamette Valley	1
34544	Willamette River, 200 feet d/s of Kellogg outfall, right bank	45.4439011	-122.645104	LASAR	Willamette Valley	Willamette	Willamette Valley	1
34545	Willamette River, 200 feet d/s of Kellogg outfall, left bank	45	-122	LASAR	Cascades	Willamette	Cascades	1
35486	Salmon River at Hatchery Below Weir Approx. USGS RM 5.05	45.0165	-123.9383	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
36341	Hillsboro Landfill SW-2	45.4995003	-122.980301	LASAR	Willamette Valley	Willamette	Willamette Valley	1
36393	Valley View (Ashland) Landfill New SW-1	42.2653999	-122.735298	LASAR	Klamath Mountains	Oregon-Washington Coastal	Coastal	1
36394	Valley View (Ashland) Landfill New SW-2	42.2626	-122.735603	LASAR	Klamath Mountains	Oregon-Washington Coastal	Coastal	1
36415	South Coast Lumber Landfill S-3	42.0779991	-124.286697	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1
36416	South Coast Lumber Landfill S-1	42.0872002	-124.287903	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1
36417	South Coast Lumber Landfill S-2	42.0783005	-124.2911	LASAR	Coast Range	Oregon-Washington Coastal	Coastal	1

Site ID	Description	Latitude	Longitude	Data Source	EPA Level-III Ecoregion	HUC 4 Watershed	Oregon Physiographic Region	Number of samples (n=361)
36432	Alsea at Mill Creek Boat Landing	44.38478	-123.62706	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
36638	New River Near Strorm Ranch Boat Ramp	42.99661	-124.45743	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
36803	Lake Creek at Sumich Rd bridge (above Triangle Lake)	44.183883	-123.553572	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
37396	Siletz River at Moonshine Park	44.77934	-123.83257	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
37400	Siuslaw River at Siuslaw Falls Park	43.85466	-123.36403	DEQ Toxics	Willamette Valley	Oregon-Washington Coastal	Willamette Valley	2
37405	Johnson Creek upstream of golf course (Bandon)	43.0943	-124.4207	DEQ Toxics	Coast Range	Oregon-Washington Coastal	Coastal	2
USGS-14128910	COLUMBIA RIVER AT WARRENDALE, OR	45.6123396	-122.027584	USGS-NWIS	Cascades	Lower Columbia	Cascades	6
USGS-14161500	LOOKOUT CREEK NEAR BLUE RIVER, OR	44.2095708	-122.256733	USGS-NWIS	Cascades	Willamette	Cascades	33
USGS-14201300	ZOLLNER CREEK NEAR MT ANGEL, OR	45.1003982	-122.82176	USGS-NWIS	Willamette Valley	Willamette	Willamette Valley	3
USGS-14206435	BEAVERTON CREEK AT SW 216TH AVE, NR ORENCO, OR	45.5206722	-122.899547	USGS-NWIS	Willamette Valley	Willamette	Willamette Valley	3

Site ID	Description	Latitude	Longitude	Data Source	EPA Level-III Ecoregion	HUC 4 Watershed	Oregon Physiographic Region	Number of samples (n=361)
USGS-14206950	FANNO CREEK AT DURHAM, OR	45.403452	-122.754819	USGS-NWIS	Willamette Valley	Willamette	Willamette Valley	3
USGS-14211720	WILLAMETTE RIVER AT PORTLAND, OR	45.5175	-122.669167	USGS-NWIS	Willamette Valley	Willamette	Willamette Valley	5
USGS-14246900	COLUMBIA RIVER @ BEAVER ARMY TERMINAL NR QUINCY,OR	46.1812214	-123.183454	USGS-NWIS	Coast Range	Lower Columbia	Coastal	52

References Cited

Beaman, J. *EPA Freshwater Copper BLM and Missing Parameter Documents: Status.* Presentation at EPA BLM Workshop, Seattle, WA May 13-14, 2015.

DeForest, D. K. , Gensemer, Robert W., Van Genderen, Eric J. , and Gorsuch, Joseph W. Protectiveness of Water Quality Criteria for Copper in Western United States Waters Relative to Predictive Olfactory Responses in Juvenile Pacific Salmon. Integrated Environmental Assessment and Management. Volume 7, Number 3—pp. 336–347 © 2011 SETAC.

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

EPA (1995). Derivation of Conversion Factors for the Calculation of Dissolved Freshwater Aquatic Life Criteria for Metals. Environmental Research Laboratory—Duluth. Office of Research and Development.

EPA (2003). The Biotic Ligand Model: Technical Support Document for Its Application to the Evaluation of Water Quality Criteria for Copper. Office of Science and Technology. Washington, D.C., United States Environmental Protection Agency**:** 72.

EPA (2007). Aquatic Life Ambient Freshwater Quality Criteria - Copper. Office of Water, United States Environmental Protection Agency. **4304T**.

EPA (2012). Calculation of Fixed Monitoring Benchmarks for Copper at Selected Monitoring Sites in Colorado. Office of Water, United States Environmental Protection Agency. **4304T**.

EPA (2012). Development of Tools to Estimate Water Quality Parameters for the Biotic Ligand Model Office of Water, United States Environmental Protection Agency.

Hem, J. D. (1985). Study and interpretation of the chemical characteristics of natural water, Department of the Interior, US Geological Survey.

Hoatson, S. (2013). Data Validation and Qualification. Oregon Department of Environmental Quality Guidance, Oregon Department of Environmental Quality.

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

HydroQual, I. (2009). The Biotic Ligand Model Windows Interface, Version 2.2.4: User's Guide and Reference Manual. Mahwah, NJ, HydroQual, Inc.

Leenheer, J. A. and J.-P. Croué (2003). "Characterizing Aquatic Dissolved Organic Matter." Environmental Science & Technology **37**(1): 18A-26A.

McIntyre, Jenifer K., David H. Baldwin, James P. Meador and Nathaniel L. Scholz (2008). *Chemosensory Deprivation in Juvenile Coho Salmon Exposed to Dissolved Copper under Varying Water Chemistry Conditions*. Environmental Science and Technology 42: 1352-1358.

MacRae, R.K., D.E. Smith, N. Swoboda-Colberg, J.S. Meyer and H.L. Bergman. 1999. Copper binding affinity of rainbow trout (*Oncorhynchus mykiss*) and brook trout (*Salvelinus fontinalis*) gills: Implications for assessing bioavailable metal. Environ. Toxicol. Chem. 18:1180-1189.

Meyer, J.S., C.J. Boese and S.A. Collyard. 2002. Whole-body accumulation of copper predicts acute toxicity to an aquatic oligochaete (*Lumbriculus variegatus*) as pH and calcium are varied. Comp. Biochem. Physiol. Part C 133:99-109.

Meyer, J.S., R.C. Santore, J.P. Bobbitt, L.D. DeBrey, C.J. Boese, P.R. Paquin, H.E. Allen, H.L. Bergman and D.M. Di Toro. 1999. Binding of nickel and copper to fish gills predicts toxicity when water hardness varies, but free-ion activity does not. Environ. Sci. Technol. 33:913-916.

McGeer JC, Szebedinszky C, McDonald DG, and Wood CM. 2002. The role of dissolved organic carbon in moderating the bioavailability and toxicity of Cu to rainbow trout during chronic waterbrone exposure. Comp. Biochem. Physiol. C: Toxicol and Pharmacol. 133C:147-161.

National Marine Fisheries Service. Jeopardy and Destruction or Adverse Modification of Critical Habitat Endangered Species Act Biological Opinion for Environmental Protection Agency's Proposed Approval of Certain Oregon Administrative Rules Related to Revised Water Quality Criteria for Toxic Pollutants. NMFS Consultation Number: 2008/00148. August 14, 2012.

Pagenkopf, G.K. 1983. Gill surface interaction model for trace-metal toxicity to fishes: Role of complexation, pH, and water hardness. Environ. Sci. Technol. 17:342-347.

R Development Core Team (2015). R: A language and environment for statistical computing. Vienna, Austria, R Foundation for Statistical Computing.

Playle, R.C., R.W. Gensemer and D.G. Dixon. 1992. Copper accumulation on gills of fathead minnows: Influence of water hardness, complexation and pH of the gill micro-environment. Environ. Toxicol. Chem. 11(3):381-391.

Playle, R.C., D.G. Dixon and K. Burnison. 1993a. Copper and cadmium binding to fish gills: Estimates of metal-gill stability constants and modeling of metal accumulation. Can. J. Fish. Aquat. Sci. 50(12):2678-2687.

Playle, R.C., D.G. Dixon and K. Burnison. 1993b. Copper and cadmium binding to fish gills: Modification by dissolved organic carbon and synthetic ligands. Can. J. Fish. Aquat. Sci. 50(12):2667-2677.

Ryan, A. and Santore, R. HDR Consultants. (2015). *Copper BLM, IWQC, FMB…What are the tools for?* Presentation at EPA BLM Workshop, Seattle, WA May 13-14, 2015.

Santore, R.C., D.M. DiToro, P.R. Paquin, and J.S. Meyer, 2001. A Biotic Ligand Model of the Acute Toxicity of Metals. II. Application to Acute Copper Toxicity in Freshwater Fish and Daphnia. Environmental Toxicology and Chemistry 20(10):2397-2402.

Santore, R.C. *Overview of the Copper BLM*. Presentation at EPA BLM Workshop, Seattle, WA May 13-14, 2015.

Stephan, C.E., D.I. Mount, D.J. Hansen, J.H. Gentile, G.A. Chapman, and W.A. Brungs, 1985. *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses*. PB85-227049. National Technical Information Service, Springfield, Virginia. EPA.

Tobiason, S., D. DeForest, N. Lewis and R. Gensemer (2014). Potential Water Quality Criteria for Copper in Oregon State Fresh Waters based on the Biotic Ligand Model. SETAC Annual Meeting, Vancouver, British Columbia, Canada.

USGS (1999). New Reporting Procedures Based on Long-Term Method Detection Levels and Some Considerations for Interpretations of Water-Quality Data Provided by the U.S. Geological Survey National Water Quality Laboratory. Open File Report 99-193, U.S. Geological Survey.

USGS (variously dated). National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations. Book 9. available online at http://pubs.water.usgs.gov/twri9A, U.S., Geological Survey.