Aluminum Aquatic Life Standard Missing Parameters Document

By: Kaley Major

June 2021

 Water Quality Standards

 700 NE Multnomah St.

 Suite 600

 Portland, OR 97232

 Phone: 503-229-5696

 800-452-4011

 Fax: 503-229-6124

www.oregon.gov/DEQ

DEQ is a leader in restoring, maintaining and enhancing the quality of Oregon's air, land and water.



This report prepared by:

Oregon Department of Environmental Quality 700 NE Multnomah Street, Suite 600 Portland, OR 97232 1-800-452-4011 www.oregon.gov/deq

Contact:

Debra Sturdevant 503-229-6691

Kaley Major 503-229-6121

DEQ can provide documents in an alternate format or in a language other than English upon request. Call DEQ at 800-452-4011 or email <u>deqinfo@deq.state.or.us</u>.

Table of Contents

Executive Summary	4
1. Introduction	6
2. Data Acquisition and Processing	7
2.1 Data Sources and Quality Assurance	7
2.2 Treatment of Censored Data	7
2.3 Methodology for using Data	8
2.3.1 Dissolved and Total Hardness Dataset	8
2.3.2 Total Hardness and Specific Conductance Dataset	9
2.3.3 Default DOC Dataset	9
2.3.4 Default Aluminum Criteria Dataset	9
3. Using Dissolved Hardness as an Estimate for Total Hardness	10
4. Estimating Total Hardness from Specific Conductivity	12
5. Default DOC Input Values	15
6. Default Aluminum Criteria	18
7. Summary	23
8. References	23
Appendix: Federal Criteria Statement (EPA 2021a)	24
Appendix: Default DOC Percentiles and Protection Evaluation Metrics	25

Executive Summary

The aluminum aquatic life criteria include a calculator that generates instantaneous criteria values (ICVs) (i.e. calculator outputs) based on the water chemistry conditions at a specific location and time. The criteria values vary with changes in water chemistry and are calculated using the input parameters pH, dissolved organic carbon (DOC), and total hardness. This document provides support and data analysis details for the DEQ's *Aluminum Standard Interpretation and Application Procedures* (ODEQ 2020), which contains specific guidance for applying the aluminum aquatic life criteria, including when one or more input parameters are missing. Specifically, this report describes the analyses used to produce estimates of missing input parameters or to calculate default values for applying the aluminum standard in Oregon.

In the absence of measured data, DEQ establishes and provides support for two different methods of estimating the input parameter of total hardness while applying the aluminum aquatic life standard in this document First, following DEQ's technical support document for implementing the copper biotic ligand model (Cu-BLM), DEQ will use dissolved hardness data when total hardness is unavailable or cannot be directly calculated from total calcium and magnesium ion concentrations (see section 3 of this document for supporting information for this decision)

The second method for estimating total hardness applies in cases where no total or dissolved hardness data are available. DEQ provides for an equation to estimate total hardness from specific conductance in cases where specific conductance data are available but hardness (or calcium and magnesium) is not. See section 4 of this document for information on the method used to derive Equation 1.

Total Hardness = $exp^{(1.050*[ln(SpC)] - 1.211)}$

Equation 1. Total hardness is measured in units of mg/L. "SpC" is a measurement of specific conductance in μ mhos/cm, "ln" is the natural logarithm, and "exp" is a mathematical constant that is the base of the natural logarithm (≈ 2.71828).

In the absence of data and estimation methods, DEQ will rely on default input parameter values (when DOC has not been measured and cannot be estimated) or default ecoregional criteria (when either pH or total hardness are missing and cannot be estimated). These conservative regional default values have been developed to ensure that Oregon's waters are protected against aluminum toxicity at least 90% of the time.

As established in Oregon's copper standard (OAR 340-041-0033 Table 30; Endnote N), when DOC is unavailable, Oregon will use total organic carbon (TOC) multiplied by the statewide conversion factor of 0.83 to estimate the input parameter of dissolved organic carbon (DOC). For cases where DOC is the only aluminum criteria calculator input parameter missing and it cannot be estimated from TOC, DEQ will use a georegional default DOC input value, similar in concept to those used in implementing the copper aquatic life criteria. These defaults are based on conservative percentiles of the DOC distributions in each georegion. The aluminum aquatic life criteria require different default DOC percentiles compared those used for copper criteria calculation in order to ensure sufficient protection for aquatic life (**Table 1**). See section 5 of this document for information on the method used to derive these default DOC values.

Table 1. Georegional default DOC percentiles and values for calculating aluminum criteria in Oregon						
Georegion	Default DOC Percentile	Default DOC Value (mg/L)				
Willamette Valley	15 th	0.83				
Coastal	30 th	0.85				
Cascades	20 th	0.48				
Eastern	15 th	0.83				
Columbia River	10 th	1.37				

Due to the complexity (e.g. non-monotonic) of the effects of pH and total hardness on aluminum toxicity and thus criteria values, DEQ chose not to develop default input values for pH or total hardness. In cases where either sufficient pH or total hardness are unavailable and cannot be estimated, DEQ will rely on default aluminum criteria values based on the 10th percentile of the distribution of all observed criteria in EPA Level III ecoregions (EPA 2021b) with the Columbia River mainstem analyzed as a separate region (**Table 2**). Due to the prevalence of pH and hardness or specific conductance data, DEQ expects the need to apply the default ecoregional aluminum criteria will be rare. See section 6 of this document for information on the methodology used to derive these default aluminum criteria values.

Table 2. Ecoregional default aluminum criteria values for Oregon						
	Default	Default	Default			
	Criteria	Acute	Chronic			
Level III Ecoregion	Percentile	Criterion	Criterion			
		(CMC ^{<i>a</i>}) μ g/L	$(\text{CCC}^{b}) \mu g/L$			
Coast Range		580	300			
Klamath Mountains		1500	770			
Willamette Valley		830	440			
Cascades		360	210			
Eastern Cascades Slopes and Foothills	10 th	1100	620			
Columbia Plateau	10	1400	800			
Blue Mountains		1200	740			
Snake River Plain		2900	1200			
Northern Basin and Range		1300	680			
Columbia River ^c		1600	750			

^a The CMC is applied as a 1-hour average, not to be exceeded more than once every three years on average.

^b The CCC is applied as a 4-day average, not to be exceeded more than once every three years on average.

^c The Columbia River mainstem is not a Level III Ecoregion, but has been analyzed as a separate region.

1. Introduction

The EPA has promulgated aluminum freshwater aquatic life criteria for Oregon. In 2004, Oregon revised its aquatic life criteria for aluminum based on EPA's 1988 recommended 304(a) criteria, which were EPA's most recent criteria recommendations at that time. In 2013, EPA disapproved the aluminum criteria submission from the state, and in 2015, EPA was subsequently sued for failing to promptly promulgate replacement criteria. In 2016, a federal consent decree established that EPA must approve or promulgate aluminum criteria for Oregon by December 31, 2020. The rule became effective on April 19, 2021 (EPA 2021a), and the criteria statement from that rule may be found as an appendix in this document for convenience (See Appendix: Federal Criteria Statement).

The aluminum criteria for Oregon are based on EPA's 2018 national recommended freshwater aquatic life criteria for aluminum (EPA 2018). The 2018 national recommended freshwater aquatic life criteria for aluminum includes the Aluminum Criteria Calculator based on multiple linear regression models and species sensitivity distributions. This calculator produces instantaneous criteria values (ICV) that account for changes in toxicity of aluminum to aquatic life due to differences in water chemistry. The aluminum criteria calculator uses three water quality parameters (referred to as "input parameters") to calculate acute and chronic ICVs that represent aluminum toxicity under the inputted water chemistry conditions. The input parameters are pH, dissolved organic carbon (DOC), and total hardness collected concurrently from the same location. While DEQ collects all three parameters when making aluminum measurements, there may be historic instances where one or more parameters is missing for a given location and time.

This document describes DEQ's methods and supporting analyses for dealing with missing input parameters for the aluminum aquatic life criteria. DEQ's approach for determining aluminum application procedures is largely consistent with the procedures used to apply the copper aquatic life criteria (ODEQ 2016). However, DEQ has adjusted some recommendations (e.g. default DOC percentiles) for aluminum implementation compared with those used for copper implementation in order to ensure that DEQ's handling of missing parameters is protective against aluminum toxicity to aquatic life.

DOC is the only input parameter that increases monotonically with aluminum criteria (i.e. as DOC increases, aluminum criteria magnitudes also increase). Given this consistency of a response from changes in DOC, when DOC is the only input parameter missing, EPA recommends the use of default DOC input values paired with measured pH and total hardness data to determine aluminum criteria (EPA 2020). The complexity of the relationship between pH and total hardness and aluminum criteria makes it difficult to derive protective default input values for pH or total hardness. Therefore, when either pH or total hardness are missing from a sample and cannot be credibly estimated, conservative default aluminum criteria will be applied instead.

2. Data Acquisition and Processing

2.1 Data Sources and Quality Assurance

Data collected by the Oregon Department of Environmental Quality (AWQMS dataset, which includes the historical LASAR dataset) and by the USGS (NWIS dataset) were used to compile a master dataset (**Table 3**). Data were screened by the following characteristics:

- Sites within the state of Oregon.
- Samples collected during the period January 1, 2000 through April 21, 2021.
- Sites identified as fresh surface waters including lakes, rivers, streams and reservoirs.
- Samples with a high QA/QC rating or grade according to the agency of origin.
 - For DEQ, data with A or B quality grades and "final" result status.
 - For USGS, data result status was "accepted", indicating it passed with respect to USGS QA/QC criteria.
- Sampling events with at least one aluminum criteria calculator input parameter (dissolved organic carbon (DOC), pH, total hardness), total organic carbon (TOC), dissolved hardness, calcium (total or dissolved), magnesium (total or dissolved), or specific conductance.
- Specific conductance less than 1500 µmhos/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.
- Grab sample data. When both field and laboratory data were provided for the same sample, field measurements were used preferentially to best represent ambient water quality conditions. This dataset was compiled, in part, to calculate default aluminum criteria values, with paired DOC, total hardness, and pH measurements collected at the same location, date, and time, as in a similar analysis performed by EPA (EPA 2019a, 2019b). Continuous measurements of pH were omitted because they were unlikely to be paired with other aluminum criteria calculator input parameters in the same place, date, and time.

Table 3. Parameters from Oregon measurements included in the master dataset				
Parameter	Parameter Type			
pH	Aluminum Criteria Calculator Input			
Organic carbon (DOC)	Aluminum Criteria Calculator Input			
Total Hardness	Aluminum Criteria Calculator Input			
Organic carbon (TOC)	To estimate DOC			
Dissolved Hardness	To estimate total hardness			
Calcium (total or dissolved)	To calculate total or dissolved hardness			
Magnesium (total or dissolved) To calculate total or dissolved hardne				
Specific Conductance	To estimate total hardness			

2.2 Treatment of Censored Data

Data were defined as censored if the measurement was at or below the Minimum Reporting Limit (MRL) of the laboratory method used to quantify the sample. Uncensored data refer to data with values above the

MRL. Censored data were included in the master dataset, but flagged because they represent measurements with a higher degree of quantification uncertainty. Censored data reporting and handling followed the procedure described in DEQ's Technical Support Document for Copper (ODEQ 2016). This procedure for treating censored data is also most amenable with data reporting in DEQ's AWQMS dataset. If a measurement was reported at the MRL, then the MRL was used as the numeric measured value, and the measurement was flagged as censored. If a measurement was reported at Minimum Detection Limit (MDL) or as a non-detect, then the MDL was used as the numeric measured value, and that measurement was flagged as censored. Occasionally, the laboratory reported an estimated concentration if a parameter was detected at a level above the MDL but below the MRL. In those cases, the estimated value was used and the sample was flagged as censored. Censored data most often took the value of the MRL using this method for assigning values. Most parameters in the master dataset had a very low proportion of censored data (< 1%) with the exception of organic carbon (18% censored; **Table 4**). To illustrate the levels of censoring, DEQ has provided more details for organic carbon, which was the parameter most affected by censoring (**Table 5**).

Table 4. Samples by parameter and censor status in the master dataset							
Parameter	Total (n)	Uncensored (n)	Censored (n)	% Censored			
рН	65,883	65,883	0	0%			
Organic carbon (DOC/TOC)	28,840	23,576	5,264	18%			
Hardness (Total or Dissolved)	6,948	6,936	12	0.17%			
Calcium (Total or Dissolved)	9,871	9,858	13	0.13%			
Magnesium (Total or Dissolved)	9,553	9,546	7	0.07%			
Specific Conductance	35,460	35,458	2	0.01%			

Table 5. Organic carbon values by censor status in the master dataset					
Censoring LevelMinimum Value (mg/L)Maximum Value (mg/L)Censored (n)% of Cens Cens Value (mg/L)					
at MRL	0.120	10.0	3,073	58%	
between MDL and MRL (estimated value)	0.258	1.90	744	14%	
at MDL	0.100	0.360	1,447	28%	

2.3 Methodology for using Data

To address the needs for substituting dissolved for total hardness, estimating total hardness from specific conductance, calculating default DOC input values, and calculating default aluminum criteria values, DEQ produced four datasets from the master dataset, each with slightly different characteristics. The methodology used to build each dataset is listed below.

2.3.1 Dissolved and Total Hardness Dataset

The Dissolved and Total Hardness dataset was compiled by selecting paired dissolved and total hardness data from the master dataset collected from the same location, date, and time with the following characteristics:

- Uncensored measurements of dissolved and total hardness.
 - If hardness was not reported, but paired (dissolved or total) calcium and magnesium were measured, hardness was calculated using the equation:

Hardness = $2.497*[Ca^{2+}] + 4.1189*[Mg^{2+}]$, where calcium and magnesium concentrations were either total or dissolved fractions and all values were in mg/L

2.3.2 Total Hardness and Specific Conductance Dataset

The Total Hardness and Specific Conductance dataset was compiled by selecting paired total hardness and specific conductance measurements from the master dataset collected from the same location, date, and time with the following characteristics:

- Uncensored measurements of total hardness, calcium, magnesium, or specific conductance.
 - If hardness was not reported, but paired total calcium and magnesium were measured, total hardness was calculated using the equation:

Total Hardness = $2.497*[Ca^{2+}] + 4.1189*[Mg^{2+}]$, where calcium and magnesium concentrations were total fractions and all values were in mg/L.

2.3.3 Default DOC Dataset

The Default DOC dataset was compiled by selecting organic carbon measurements from the master dataset with the following characteristics:

- Censored and uncensored dissolved (DOC) or total (TOC) organic carbon measurements.
- In cases where DOC data were unavailable, but TOC was available, DOC was estimated by multiplying TOC by 0.83 as established in Oregon's Cu-BLM TSD (ODEQ 2016).
 - However, if DOC was a censored measurement but TOC was not, then DOC was estimated by multiplying TOC by 0.83.

2.3.4 Default Aluminum Criteria Dataset

The Default Aluminum Criteria dataset was compiled by selecting data from the master dataset collected from the same location, date, and time with the following characteristics:

- Censored and uncensored measurements of pH, DOC, TOC, hardness, calcium, magnesium, or specific conductance.
- In cases where DOC data were unavailable, but TOC was available, DOC was estimated by multiplying TOC by 0.83 as established in Oregon's Cu-BLM TSD (ODEQ 2016).
 - However, if DOC was a censored measurement but TOC was not, then DOC was estimated by multiplying TOC by 0.83.
- Total (unfiltered) hardness data were used preferentially, but dissolved (filtered) hardness data were used when total hardness was not available (see section 3 below).
 - If hardness was not reported, but calcium and magnesium were measured, hardness was calculated using the equation:
 - Hardness = $2.497*[Ca^{2+}] + 4.1189*[Mg^{2+}]$, where calcium and magnesium concentrations were either total or dissolved fractions and all values were in mg/L
 - If calcium and magnesium were not measured, total hardness was estimated using the relationship between hardness and specific conductance:

Total Hardness = $\exp^{(1.050*[\ln(SpC)] - 1.211)}$ (see section 4 below).

3. Using Dissolved Hardness as an Estimate for Total Hardness

When total hardness measurements (or total calcium and magnesium concentrations) are not reported, DEQ sometimes utilizes dissolved hardness (or dissolved calcium or magnesium concentrations) instead. To demonstrate that the relationship between dissolved and total hardness is strong and that the variables may be used interchangeably with a minimal effect on aluminum criteria, DEQ used the Dissolved and Total Hardness dataset (see section 2 for details). In this dataset, a sample consisted of paired, uncensored dissolved and total hardness measurements for a given location, date, and time (**Table 6**).

Table 6. Summary statistics for parameters used to establish the relationship between dissolved and total hardness						
Sample Parameter Parameter Units n Minimum Mean Median Maximum						Maximum
Dissolved Hardness	mg/L CaCO ₃	1,070	6.99	62.68	39.75	589
Total Hardness mg/L CaCO ₃ 1,070 7.22 63.69 40.20 593						

DEQ used Spearman's rank correlation (ρ), a non-parametric method of statistical dependence, to evaluate the relationship between dissolved and total hardness. A positive value near 1 indicates a strong positive correlation. DEQ found the correlation between dissolved and total hardness was strong and positive ($\rho = 0.996$).

DEQ used ordinary least-square regression (OLS) to establish a linear relationship between dissolved and total hardness data. This resulted in a high adjusted R^2 value (0.998) and low root mean square error (RMSE = 3.41 mg/L) (Figure 1; Table 7). The strong and positive relationship between dissolved and total hardness and a simple linear regression equation with a slope of 1.0 provide support for using dissolved hardness as an estimate of total hardness for instances in which total hardness is unavailable.

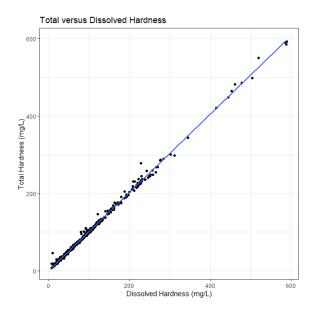
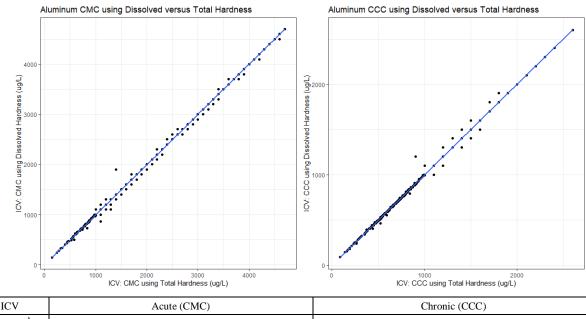


Figure 1. Linear regression for total hardness vs. dissolved hardness in Oregon during the period 2000 through 2021. The blue line represents linear relationship of best fit.

Table 7. Total versus dissolved hardness Spearman's rank correlation statistic and regression equation information from Oregon data in the Dissolved and Total Hardness Dataset				
Spearman's rank correlation (ρ) 0.996				
Regression equation	Total Hardness = 1.0123(Dissolved Hardness)–0.2415			
Adjusted R ² value 0.998				
p-value < 2.2e-16				
RMSE	3.41 mg/L			

To evaluate the effect of using dissolved hardness instead of total hardness on resulting aluminum criteria values, DEQ used a measured dataset of 1,070 concurrent measurements of pH, DOC, total hardness, and dissolved hardness (a subset of the Default Aluminum Criteria dataset, see section 6 below) to compare calculated criteria output values using total hardness to those calculated by substituting dissolved hardness values instead (**Figure 2**). Strong positive Spearman's rank correlation coefficient ($\rho = 0.999$), regression equations with high adjusted R² values (0.998, 0.999), and low root mean square error (RMSE $\leq 31 \ \mu g/L$) provide strong support that dissolved hardness may be used as a substitute for total hardness in Oregon waters with a minimal effect on output criteria values. Thus, DEQ will use dissolved hardness as an estimate for total hardness when implementing the aluminum aquatic life standard if total hardness is not available.



ICV	Acute (CMC)	Chronic (CCC)
Spearman's rank correlation (ρ)	0.999	0.999
Equation	$ICV_{Disolved Hardness} = 1.000(ICV_{Total Hardness})$ -4.643	$ICV_{Disolved Hardness} = 1.003(ICV_{Total Hardness}) - 2.702$
Adjusted R ²	0.999	0.998
p-value	< 2.2e-16	< 2.2e-16
RMSE	31 µg/L	17 µg/L

Figure 2. Comparison of ICVs calcultaed using dissolved hardness data with those calculated using total hardness data for both the acute (CMC) and chronic (CCC) aluminum criteria calculator outputs.

4. Estimating Total Hardness from Specific Conductivity

When hardness measurements or calcium and magnesium concentrations were not reported, an equation to estimate total hardness from specific conductivity was established using data in the Total Hardness and Specific Conductance dataset (see section 2 for details). In this dataset, a sample consisted of paired, uncensored total hardness and specific conductance measurements for a given location, date, and time (**Table 8**).

Table 8. Summary statistics for parameters used to establish the relationship between total hardness and specific						
conductance						
Sample Parameter Parameter Units n Minimum Mean Median Maximu						Maximum
Total Hardness mg/L CaCO ₃ 836 6.5 49.1 36.6 261						
Specific Conductance	µmhos/cm at 25°C	836	24.0	127.1	100	666

DEQ performed a similar analysis in the Cu-BLM TSD, in which hardness and specific conductance were found to be highly correlated in Oregon waters (ODEQ 2016). The relationship between these variables was reassessed during the aluminum standard analysis to specify the relationship between *total* hardness and specific conductance for current conditions in Oregon ambient waters.

DEQ found the correlation between total hardness and specific conductance was strong and positive ($\rho = 0.993$), which was slightly higher than the correlation from a similar analysis DEQ performed for the copper standard using median site values to establish a strong positive correlation between hardness and specific conductance ($\rho = 0.97$) (ODEQ 2016).

DEQ used ordinary least-square regression (OLS) to establish a linear relationship between total hardness and specific conductance data. As in the Cu-BLM TSD (ODEQ 2016), natural-log transformed data provided a higher adjusted R² value (0.986 versus 0.980) and lower root mean square error (0.102 versus 6.47 mg/L) compared with non-transformed data, indicating a better model fit for the natural-log transformed data (**Figure 3**). The natural-log transformed data were used to establish the equation that DEQ will use to estimate total hardness from specific conductance in cases where total and dissolved hardness are unavailable (**Table 9**). The relationship established between total hardness and specific conductance during the aluminum standard analysis was very similar to the one established between hardness and specific conductance previously during the copper analysis¹.

¹ The Cu-BLM TSD (ODEQ 2016) established the following relationship:

 $ln(Hardness) = 1.02 \cdot ln(Specific Conductance) - 1.16.$

Hardness in was measured in mg/L as CaCO₃, specific conductance in μ mhos/cm at 25°C. "ln" is the natural log.

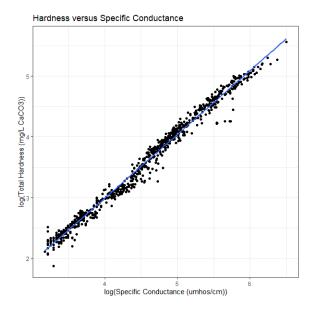
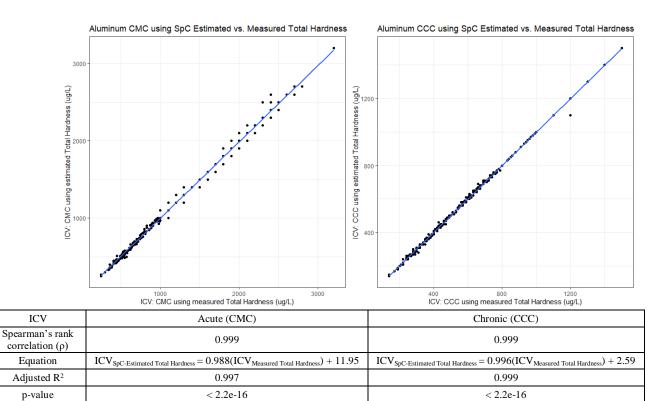


Figure 3. Natural-log transformed total hardness vs. natural-log transformed specific conductance in Oregon during the period 2000 through 2021. The blue line represents linear relationship of best fit.

Table 9. Total hardness vs. specific conductance Spearman's rank correlation statistic and regression equation information from Oregon data in the Total Hardness and Specific Conductance				
	dataset.			
Spearman's rank correlation (ρ) 0.993				
Regression equation $ln(Total Hardness) = 1.050 \cdot ln(Specific Conductance) - 1.050 \cdot ln(Specific$				
Adjusted R ² value	0.986			
p-value < 2.2e-16				
RMSE	0.102 mg/L			

DEQ evaluated the effect that estimating total hardness from specific conductance had on aluminum criteria compared to criteria generated using measured total hardness. To perform this evaluation, DEQ used paired samples from the Default Aluminum Criteria Dataset (see section 6 below), where both specific conductance and total hardness were available. A total of 403 samples with paired pH, DOC (measured or estimated), total hardness and specific conductance measured at the same location, date, and time were available for this analysis.

Linear regressions between ICVs calculated using specific-conductance estimated total hardness and measured total hardness were strong with slopes near 1.0 (0.988 for the CMC and 0.996 for the CCC). Regressions indicated high correlations (0.999) and adjusted R² values (0.997, 0.999) as well as low RMSE ($\leq 41 \ \mu g/L$) relative to the scale of the criteria for both the CMC and CCC (**Figure 4**). The aluminum criteria are not strongly affected by estimating total hardness using specific conductance. Thus, DEQ will use specific conductance to estimate total hardness in the absence of other hardness data during the implementation of the aluminum standard.



 $41 \, \mu g/L$ 9.6 µg/L Figure 4. Comparison of ICVs calcultaed using total hardness data estimated using specific conducatnce with those calculated using measured hardness data for both the acute (CMC) and chronic (CCC) aluminum criteria value calculator outputs.

RMSE

5. Default DOC Input Values

Of the three input parameters used to calculate aluminum criteria, DOC is the only one that has a direct and positive relationship with the calculator output values (i.e. as DOC increases, aluminum criteria increase). As such, in cases where pH and hardness are available for a given sample, but when DOC is missing, EPA recommends inputting default DOC values for use in the aluminum criteria calculator (EPA 2018). DEQ uses Oregon georegional default DOC values as inputs to the Copper Biotic Ligand model (15th percentile DOC for Eastern georegion, 20th percentile for all other georegions; OAR 340-041-8033). These georegions were created by grouping EPA Level III ecoregions using similarities in water quality parameters, including DOC (ODEQ 2016). For consistency with copper standard implementation procedures (ODEQ n.d.), DEQ will also use default DOC input values based on georegional percentiles for aluminum standard implementation (ODEQ 2020). Georegional DOC data within the Default DOC dataset (see section 2 for details) from 1,782 sites in Oregon (**Table 10**) were used to generate DOC distributions (**Figure 5**) for each of the five Oregon georegions.

Table 10. Summary statistics for Oregon DOC measurements from the Default DOC dataset							
	n			DOC (mg/L)			
Georegion	Samples	Sites	Minimum	Mean	Median	Maximum	
Cascades	1,445	261	0.083	1.00	0.83	14.94	
Coastal	5,689	469	0.083	1.82	1.66	99.60	
Columbia River	194	22	0.83	3.97	1.66	246.51	
Eastern	7,389	626	0.083	4.06	3.10	79.60	
Willamette Valley	6,981	404	0.083	2.52	1.70	132.00	
Statewide	21,698	1,782	0.083	2.77	1.66	246.51	

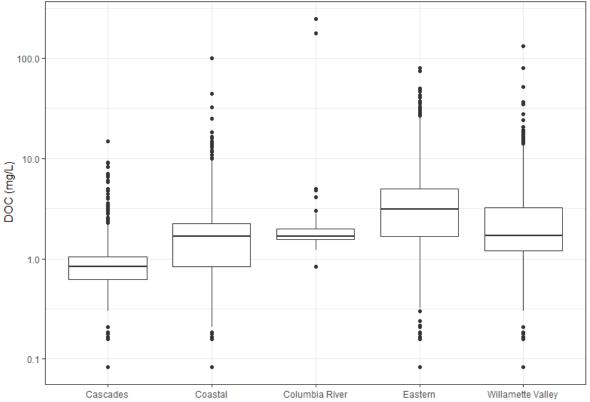


Figure 5. Boxplots of DOC (measured and estimated) from the Default DOC dataset, by georegion. Boxes are comprised of 25th, 50th and 75th percentile boundaries. Upper and lower whiskers represent the highest and lowest measurements within 1.5 times the interquartile range. Points above upper whiskers or below lower whiskers are outliers.

EPA performed an analysis to determine the impact of using regional default DOC input values based on a variety of percentiles on the protectiveness of subsequently generated aluminum criteria (EPA 2019a). EPA defined protective conditions in the analysis by the following:

- The default-DOC based criteria values were lower than measured numeric criteria values at least 90% of the time.
- The 90th percentile of the ratio between the default DOC-based and measured criteria values (the criteria magnitude ratio (CMR)) was less than or equal to 1.0.

DEQ used EPA's approach for determining default DOC protectiveness. To determine default DOC input value protectiveness, DEQ used a measured dataset of 4,008 concurrent measurements of pH and measured or estimated DOC and total hardness described below (see section 6 below) to compare calculated criteria output values from measured (or estimated) data to those calculated by substituting default DOC values on a georegional basis. DEQ explored using default DOC percentiles ranging from the 5th percentile to the 35th percentile for each georegion. The full range of default DOC percentiles and corresponding evaluation metrics (percent protection and 90th percentile CMR) can be found in the Appendix: Default DOC Percentiles and Protection Evaluation Metrics.

DEQ found that using the 10th percentile for the Columbia River mainstem, the 15th percentile for the Willamette Valley and Eastern georegions, the 20th percentile for the Cascades georegion, and the 30th percentile for the Coastal georegion provided a sufficient level of percent protectiveness (89% to 98%)

and georegional 90th percentile CMRs at or below 1.0. (**Table 11**). Thus, DEQ will use the default DOC values provided in Table 11 to implement the aluminum standard in Oregon.

Table 11. Oregon's georegional default DOC input parameter percentiles, values, and evaluation metrics for aluminum								
	Defaults		Georegional Protection Analysis					
Georegion			Acute	(CMC)	Chronic (CCC)			
	Default DOC Percentile	Default DOC Input Value (mg/L)	% Protection	90 th Percentile CMR ^{<i>a</i>}	% Protection	90 th Percentile CMR ^{<i>a</i>}		
Willamette Valley	15 th	0.83	97%	1.00	97%	1.00		
Coastal	30 th	0.85	92%	1.00	89%	1.02		
Cascades	20 th	0.48	91%	0.98	91%	0.98		
Eastern	15 th	0.83	98%	1.00	96%	1.00		
Columbia River	10 th	1.37	92%	1.00	94%	1.00		

^{*a*} The Criteria Magnitude Ratio is the ratio between the default DOC-based and measured criteria values for a given sample.

6. Default Aluminum Criteria

The complex relationship between pH, total hardness, and aluminum criteria magnitudes makes it difficult to calculate conservative default pH or total hardness input parameter values that would protect against aluminum toxicity. Instead, EPA recommends the use of default aluminum criteria values when pH or total hardness measurements are missing and cannot be estimated for a sample (EPA 2020). DEQ's Default Aluminum Criteria dataset (see section 2 for details) contained 4,008 concurrent measurements of pH and measured estimated DOC and total hardness from a total of 512 sites in Oregon (**Figure 7**). DEQ evaluated default aluminum criteria by EPA Level III ecoregion (EPA 2021b), with the Columbia River mainstem designated as a separate region.-.

DEQ examined the distribution of sites with paired aluminum criteria calculator input data and determined that while some ecoregions had more sites and samples than others, the sites were well distributed across the state and within ecoregions (**Figure 7**). DEQ used the data available in the Default Aluminum Criteria dataset to generate both acute (CMC) and chronic (CCC) aluminum ICV distributions for each ecoregion (**Figure 8**).

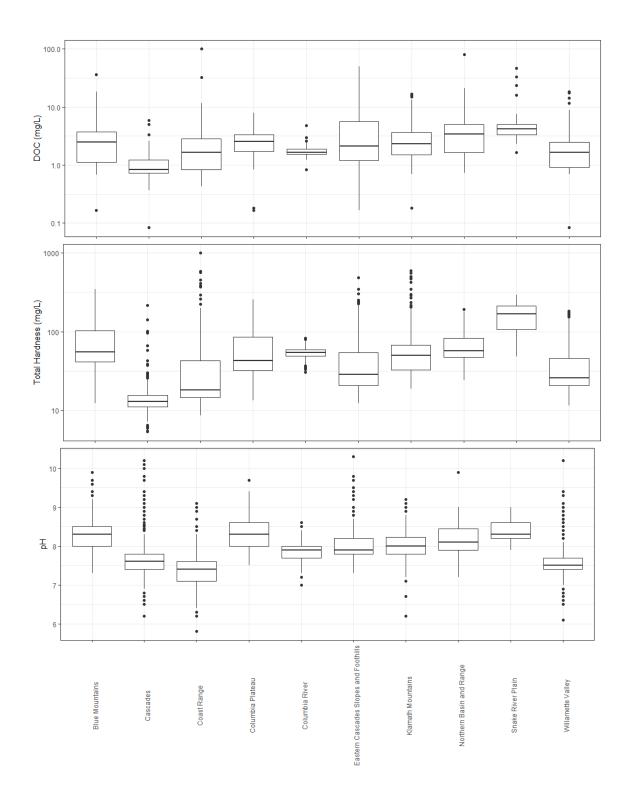


Figure 6. Boxplots of input parameter data from the Default Aluminum Criteria dataset used to calculate default aluminum criteria by Level III Ecoregion with the Columbia River mainstem treated separately. DOC and total hardness were measured or estimated while pH was measured only. Boxes are comprised of 25th, 50th and 75th percentile boundaries. Upper and lower whiskers represent the highest and lowest measurements within 1.5 times the interquartile range. Points above upper whiskers or below lower whiskers are outliers.

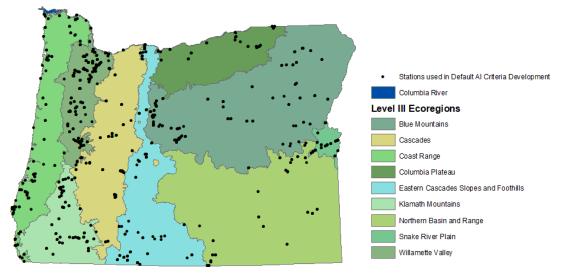


Figure 7. Sites in Oregon with concurrently measured pH and measured or estimated DOC and total hardness input parameter data that were used in default aluminum criteria development.

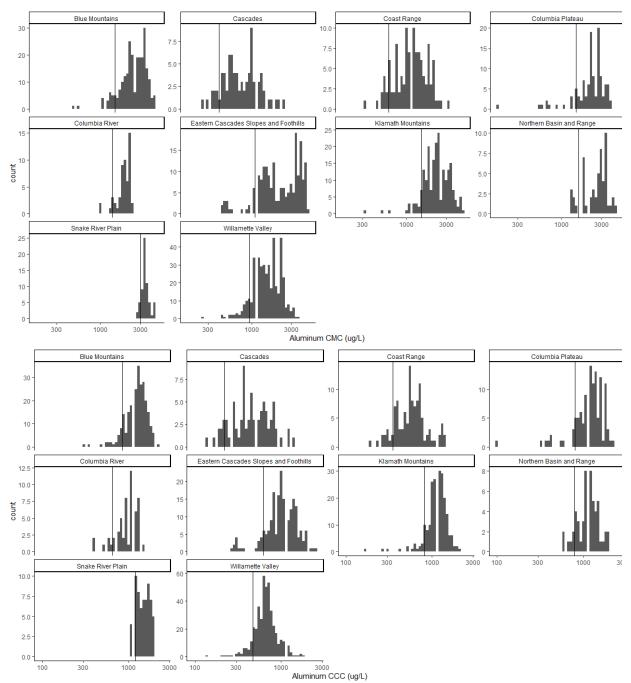


Figure 8.: Distribution of aluminum acute (CMC) and chronic (CCC) ICVs by Level III Ecoregion with the Columbia River mainstem calculated separately. Vertical lines are 10th percentile criteria values for each region.

EPA performed an analysis using Oregon data that recommended establishing default criteria at the 5th or 10th percentile of each ecoregional distribution to ensure that default aluminum criteria were protective, depending on the treatment of censored data (EPA 2019b). EPA defined protective conditions in the analysis by the following:

- The default criteria values were lower than measured numeric criteria values at least 90% of the time.
- The 90th percentile of the ratio between the default criteria values and measured criteria values (the criteria magnitude ratio (CMR)) was less than or equal to 1.0.

DEQ used EPA's approach for determining default aluminum criteria protectiveness. DEQ calculated the 10th percentile of aluminum criteria by ecoregion (with the Columbia River calculated separately) as a conservative default, using bootstrapping with 10,000 replicates to establish 95% confidence intervals. DEQ found that default aluminum criteria based on the10th percentile provided a high level of percent protectiveness (90% to 92%) and 90th percentile CMRs at or below 1.0 (0.98 to 1.01) depending on the ecoregion (**Table 12**). Thus, aluminum criteria set at the 10th percentile by ecoregion represent conservative default values for Oregon waters, and DEQ will use these values during implementation of the aluminum standard when pH or total hardness are unavailable.

Table 12. Ecoregional aluminum default criteria (10th percentile) and evaluation metrics												
	n		Acute				Chronic					
Level III Ecoregion			Default Acute Aluminum Criteria (CMC) µg/L		Default CMC Protection Metrics		Default Chronic Aluminum Criteria (CCC) µg/L		Default CCC Protection Metrics			
	Samples	Sites	CMC a	95 Confi Inte	dence	% Protect	90 th Percentile CMR ^b	CCCC	95 Confi Inte	dence	% Protec	90 th Percentile CMR ^b
Coast Range	399	100	580	520	630	90%	1.00	300	270	330	90%	1.01
Klamath Mountains	244	47	1500	1400	1700	90%	1.00	770	710	860	90%	1.00
Willamette Valley	1740	125	830	790	870	90%	1.00	440	430	460	90%	1.00
Cascades	489	38	360	280	420	90%	1.00	210	180	240	90%	1.00
Eastern Cascades Slopes and Foothills	260	47	1100	1000	1300	92%	1.00	620	560	670	90%	1.00
Columbia Plateau	118	23	1400	1200	1800	90%	0.98	800	690	1000	90%	1.00
Blue Mountains	434	76	1200	1100	1300	91%	1.00	740	710	830	90%	1.00
Snake River Plain	102	19	2900	2800	3100	90%	1.00	1200	1200	1300	92%	1.00
Northern Basin and Range	91	29	1300	1100	1400	92%	1.00	680	540	750	91%	1.00
Columbia River ^d	131	8	1600	1400	1800	92%	1.00	750	720	890	91%	1.00

^a The CMC is applied as a 1-hour average, not to be exceeded more than once every three years on average.

^b The Criteria Magnitude Ratio is the ratio between the default aluminum and measured criteria values for a given sample.

^cThe CCC is applied as a 4-day average, not to be exceeded more than once every three years on average.

^d The Columbia River mainstem is not an ecoregion but was analyzed as separate region.

7. Summary

In this document, DEO provides information about the data analyses performed to support the DEO's Aluminum Standard Interpretation and Application Procedures (ODEO 2020). This includes a description of data handling and use, support for the decision to use dissolved hardness as an estimate of total hardness when total hardness input parameter data for the aluminum criteria calculator are unavailable, an equation for estimating total hardness from specific conductivity when total and dissolved hardness are unavailable, default DOC input values (when DOC is the only aluminum input parameter missing), and default aluminum criteria values (when either pH or measured or estimated total hardness input parameters are missing). While these approaches are generally consistent with DEO's implementation of the copper BLM in Oregon, DEQ has adjusted its approach to ensure that implementation of the aluminum aquatic life criteria provide sufficient protection in Oregon waters. For example, DEQ has changed the default DOC input percentiles compared to those used for the copper standard for select georegions based on an independent analysis of protectiveness. Further, DEQ has elected not to use default input parameter values for pH or total hardness, given the complexity of the relationship between pH, total hardness, and the aluminum criteria. Instead DEQ is electing to use conservative default aluminum criteria when either pH or total hardness have not been measured or estimated. DEQ encourages concurrent measurements of pH, total hardness, and DOC during data collection, while relying on defaults primarily for evaluation of historical aluminum concentrations where the input parameter data are not available.

8. References

- EPA. 2018. *Final Aquatic Life Ambient Water Quality Criteria for Aluminum 2018*. EPA-822-R-18-001. Washington, D. C.: U.S. Environmental Protection Agency, Office of Water.
- EPA. 2019a. Analysis of the Protectiveness of Default Dissolved Organic Carbon Options.
- EPA. 2019b. Analysis of the Protectiveness of Default Ecoregional Aluminum Criteria Values.
- EPA. 2020. Draft Technical Support Document: Implementing the 2018 Recommended Aquatic Life Water Quality Criteria for Aluminum. U.S. Environmental Protection Agency, Office of Water.
- EPA. 2021a. Federal Aluminum Aquatic Life Criteria Applicable to Oregon.
- EPA. 2021b. Level III and IV Ecoregions of the Continental United States.
- ODEQ. 2016. Technical Support Document: An Evaluation to Derive Statewide Copper Criteria Using the Biotic Ligand Model. Oregon Department of Environmental Quality.
- ODEQ. 2020. Draft Aluminum Standard Interpretation and Application Procedures. Oregon.
- ODEQ. n.d. Implementation of the Freshwater Aquatic Life Water Quality Standards for Copper. Oregon Department of Environmental Quality.

Appendix: Federal Criteria Statement (EPA 2021a)

TABLE 1 TO PARAGRAPH (b)—ALUMINUM AQUATIC LIFE CRITERIA FOR OREGON FRESH WATERS

Metal	CAS No.	Criterion maximum concentration $(CMC)^{3} (\mu g/L)$	Criterion continuous concentration (CCC) ⁴ (µg/L)		
Aluminum ¹²	7429905	Acute (CMC) and chronic (CCC) fre site shall be calculated using the 201 (Aluminum Criteria Calculator V.2.0 software package using the same 198 underlying model equations as in the	shwater aluminum criteria values for a 8 Aluminum Criteria Calculator 0.xlsx), or a calculator in R or other 35 Guidelines calculation approach and		
		Criteria for Aluminum. ⁵			

¹To apply the aluminum criteria for Clean Water Act purposes, criteria values based on ambient water chemistry conditions must protect the water body over the full range of water chemistry conditions, including during conditions when aluminum is most toxic.

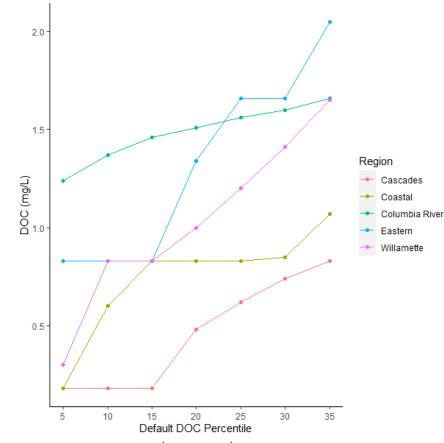
²These criteria are based on aluminum toxicity studies where aluminum was analyzed using total recoverable analytical methods. Oregon may utilize total recoverable analytical methods to implement the criteria. For characterizing ambient waters, Oregon may also utilize, as scientifically appropriate and as allowable by State and Federal regulations, analytical methods that measure the bioavailable fraction of aluminum (e.g., utilizing a less aggressive initial acid digestion, such as to a pH of approximately 4 or lower, that includes the measurement of amorphous aluminum hydroxide yet minimizes the measurement of mineralized forms of aluminum such as aluminum silicates associated with suspended sediment particles or clays). Oregon shall use measurements of total recoverable aluminum where required by Federal regulations.

³The CMC is the highest allowable one-hour average ambient concentration of aluminum. The CMC is not to be exceeded more than once every three years. The CMC is rounded to two significant figures.

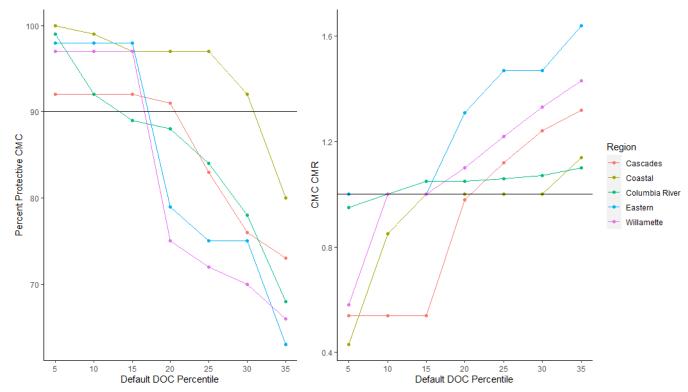
⁴The CCC is the highest allowable four-day average ambient concentration of aluminum. The CCC is not to be exceeded more than once every three years. The CCC is rounded to two significant figures.

⁵EPA–822–R–18–001, Final Aquatic Life Ambient Water Quality Criteria for Aluminum—2018, December 2018, is incorporated by reference into this section with the approval of the Director of the Federal Register under 5 U.S.C. 552(a) and 1 CFR part 51. All approved material is available from U.S. Environmental Protection Agency, Office of Water, Health and Ecological Criteria Division (4304T), 1200 Pennsylvania Avenue, NW, Washington, DC 20460; telephone number: (202) 566–1143, www.epa.gov/wqc/aquatic-life-criteria-aluminum. It is also available for inspection at the National Archives and Records Administration (NARA). For information on the availability of this material at NARA, email fedreg.legal@nara.gov or go to www.archives.gov/federal-register/cfr/ibr-locations.html.

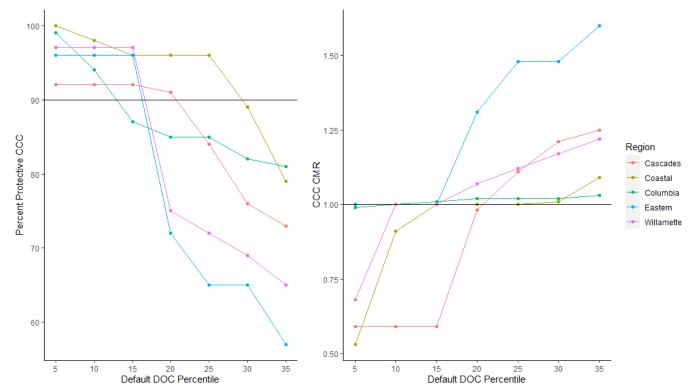
Appendix: Default DOC Percentiles and Protection Evaluation Metrics



Default DOC percentile values (5th through 35th percentiles) by georegion.



The effect of georegional default DOC percentile on protectiveness of calculated acute aluminum criteria (CMC) values. Protection of pairing default DOC values with total hardness and pH was evaluated using percent protection (left graph) and criteria magnitude ratio (CMR; right graph). A protective condition from a given default DOC percentile was defined as a percent protectiveness of 90% or greater (left horizontal line) or a CMR equal to or less than 1.00 (right horizontal line).



The effect of georegional default DOC percentile on protectiveness of calculated chronic aluminum criteria (CCC) values. Protection of preparing default DOC values with total hardness and pH was evaluated using percent protection (left graph) and criteria magnitude ratio (CMR; right graph). A protective condition from a given default DOC percentile was defined as a percent protectiveness of 90% or greater (left horizontal line) or a CMR equal to or less than 1.00 (right horizontal line).