State of Oregon Department of Environmental Quality

Aluminum Standard Interpretation and Application Procedures

Introduction

The EPA has promulgated Clean Water Act section 304(a) aluminum freshwater aquatic life criteria in Oregon. In 2004, Oregon revised its aquatic life criteria for aluminum based on EPA's1988 national criteria recommendations, which were the most recent 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 prepare and publish replacement criteria for several pollutants, including aluminum. In 2016, a federal consent decree established that EPA must approve or promulgate aluminum criteria for Oregon by December 31, 2020. The federal aluminum criteria for Oregon are based on EPA's final 2018 national recommended freshwater aquatic life criteria (EPA 2018). 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).

EPA's 2018 national recommended freshwater aluminum aquatic life criteria magnitudes are determined using 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 used to calculate an ICV should be collected at the same time and location as the aluminum sample being evaluated.

This document explains the procedures for applying and interpreting Oregon's aquatic life criteria for aluminum, including: deriving ICVs (calculator outputs) using the calculator, estimating calculator input parameters, using default input parameters when measured or estimated data are not available, and applying the default ecoregional aluminum criteria when appropriate. This document also describes DEQ's preference to use bioavailable aluminum concentration data for ambient waters.

This document does not describe how the criteria are implemented in Oregon's Integrated Report assessment, permitting or other water quality programs. Refer to DEQ's *Methodology for Oregon's 2022 Water Quality Report and List of Water Quality Limited Waters* (ODEQ 2021b) for more details on how the assessment will evaluate aluminum data, including the use of total recoverable versus bioavailable aluminum measurements. The permitting program will

separately develop procedures for conducting Reasonable Potential Analysis and establishing permit limits that will protect the site throughout the range of conditions expected to occur. These procedures are expected to be consistent with the procedures to implement the copper criteria in NPDES permits. Sufficient data must be collected to reasonably characterize the range of conditions expected to occur at the site. Multiple ICVs will be calculated for the discharge location based on the range of water chemistry conditions measured. Permit limits will be based on the 10th percentile of the ICVs, or another conservative value, in order to protect aquatic life during the most toxic conditions. See the aluminum permitting procedures for additional information.

Bioavailable aluminum data

The 2018 national recommended aluminum criteria are expressed as total recoverable aluminum because the method used to measure aluminum during the laboratory testing was total recoverable aluminum. However, laboratory waters have very low suspended solids. In the environment, aluminum is present in rocks, clays, and soils/sediments. Not all of these forms of aluminum are biologically available to aquatic species in ambient waters. In natural waters with suspended solids, total recoverable aluminum methods, which use an acid digestion method to release aluminum attached to solids, are likely to overestimate the fraction of aluminum that is toxic. In fact, a less aggressive initial digestion method may better estimate the "bioavailable" (toxic) portion of aluminum (Rodriguez et al. 2019). EPA includes a reference to the potential application of bioavailable aluminum analytical methods for ambient waters in the aluminum federal rule for Oregon freshwaters, footnote two to the criteria statement (EPA 2021a) (See Appendix for convenience).

DEQ intends to use the bioavailable aluminum method to measure the aluminum concentration in ambient waters. These bioavailable ambient aluminum data will be used in application of the aluminum criteria for purposes of water quality assessment, permitting, TMDLs and other water quality protection purposes that rely on ambient aluminum concentration data. The DEQ laboratory is adopting an analytical method to measure bioavailable aluminum (Rodriguez et al. 2019) that is nationally under development as an ASTM approved method. DEQ will report both total recoverable and bioavailable aluminum data for ambient water quality monitoring in Oregon. At this time, the bioavailable method is not approved for measuring aluminum in wastewater, such as effluent discharges.

Where bioavailable data are not available, DEQ may need to use total recoverable aluminum data until new data are collected or until DEQ is able to develop a translator to convert historic total recoverable measurements to the bioavailable fraction. However, when assessing Oregon waters, if a waterbody is exceeding the aluminum criteria but only total recoverable aluminum data are available, DEQ will place that waterbody in category 3B, rather than list it as impaired in category 5 (ODEQ 2021b). This approach is consistent with the federally promulgated aluminum rule (EPA 2021a). EPA states that:

> "The requirement to assemble and evaluate all data and information for assessment and listing purposes includes situations where only total recoverable aluminum data and information are available. However, in those circumstances, the State is not required to rely on that data for listing purposes as long as it provides a technical, science-based rationale for not using the data and information. 40 CFR 130.7(b)(6)(iii). This technical, science-based rationale documenting the State's consideration of existing and readily available data and information is referenced in the additional footnote language to the criteria statement, which speaks to Oregon's ability to use analytical methods that measure the bioavailable fraction of aluminum for characterizing ambient waters ''as scientifically appropriate.'' For example, the State may be able to demonstrate that total recoverable aluminum samples are not representative of water quality conditions because non-toxic, non-bioavailable forms of aluminum are leading to an exceedance above the criterion. When data and information are available for both total recoverable and bioavailable aluminum, the State must evaluate all of it, but need not rely on all of it for assessment and listing purposes. Applicable regulations do not prohibit the State from assigning more weight to data and information about bioavailable aluminum than total recoverable aluminum for assessment and listing purposes."

Bioavailable methods may be used for wastewater effluent only after an accepted method is approved in 40 CFR part 136 to measure and report effluent bioavailable aluminum concentrations. At this time, bioavailable aluminum methods are not available for wastewater effluent and are not an approved method for wastewater in 40 CFR part 136. Total recoverable aluminum methods shall be used for clean water act programs where required by statute.

Aluminum Criteria Calculator

The Aluminum Criteria Calculator is used to obtain ICVs based on a set of input parameter values. Aluminum bioavailability and, therefore toxicity, to aquatic life are affected by changes in water chemistry, particularly dissolved organic carbon (DOC), total hardness, and pH. The Aluminum Criteria Calculator produces the U.S. EPA 304(a) national recommended criteria magnitudes for both chronic (CCC) and acute (CMC) aluminum.

The Aluminum Criteria Calculator version 2.0 has been provided by EPA in an excel format or an R code and data format. As a convenience, you may download the excel format from the following link:
https://www.epa.gov/sites/production/files/2018-12/aluminum-criteria-calculator-v20.xlsm
or the R code and data from the following link:
https://www.epa.gov/sites/production/files/2020-01/aluminum-criteria-calculator-rcode-data.zip.

Appendix K of EPA's 2018 national recommended freshwater aquatic life criteria for aluminum contains a series of lookup tables that provide aluminum criteria magnitudes generated with the Aluminum Criteria Calculator version 2.0 for a limited number of DOC, total hardness, and pH values (EPA 2018). However, lookup tables only provide criteria for discrete increments of input parameter values and therefore do not provide sufficient information to determine criteria for all possible input parameter values.

The Water Quality Standards team at DEQ will answer questions about using the calculator. However, as the calculator was not developed by DEQ, we are not able to provide technical support for the calculator in the event that it does not function properly. In that case, please use the contact listed on the U.S. EPA Final Aquatic Life Ambient Water Quality Criteria for Aluminum 2018 for more information (EPA 2018).

Procedures to calculate Instantaneous Criteria Values (ICVs)

Calculation of an ICV in ambient waters requires input of the following water quality parameters, measured concurrently. If there is an aluminum measurement being evaluated, that measurement should also be measured concurrently with the input parameters. DEQ now measures all the input parameters with each aluminum sample collected. However, there are historic aluminum measurements or third party data measurements where the input parameters were not measured concurrently. Therefore, this section also provides procedures to derive and apply the criteria for ambient waters if all of the input parameters were not measured concurrently. For permitting applications, refer to the permitting implementation procedures, which explain how to conduct reasonable potential analysis given that the water chemistry downstream of a discharge may be altered by the effluent.

PARAMETERS
Dissolved organic carbon (DOC) (mg/L)
pH (Standard Units)
Total Hardness (mg/L $CaCO_3$)

Organic carbon should be measured as the dissolved form and should be filtered and analyzed according to a standard analytical method. Samples passing a 0.45μm filter are considered dissolved for these purposes. Total hardness should be measured without filtration.

The following procedures and process flow chart (Figure 1) should be used to determine whether the ICVs can be calculated based on available data or default input values, or a default aluminum criterion must be applied to evaluate an aluminum measurement.

1. Determine the availability of organic carbon measurements.
    a. If measured as DOC, enter this value.
    b. If measured as TOC, apply a correction factor of 0.83 to estimate the concentration as DOC. Enter this value.
    c. If neither DOC nor TOC were measured and DOC is the only missing input parameter, enter the appropriate **georegional default DOC value** from Table 1 below.

2. Determine the availability of pH measurements.
    a. If pH has been measured, enter this value.
    b. If pH has not been measured, apply a representative value based on pH data collected at other times at the site, and/or data from a nearby representative monitoring location. DEQ will use professional judgement to determine whether

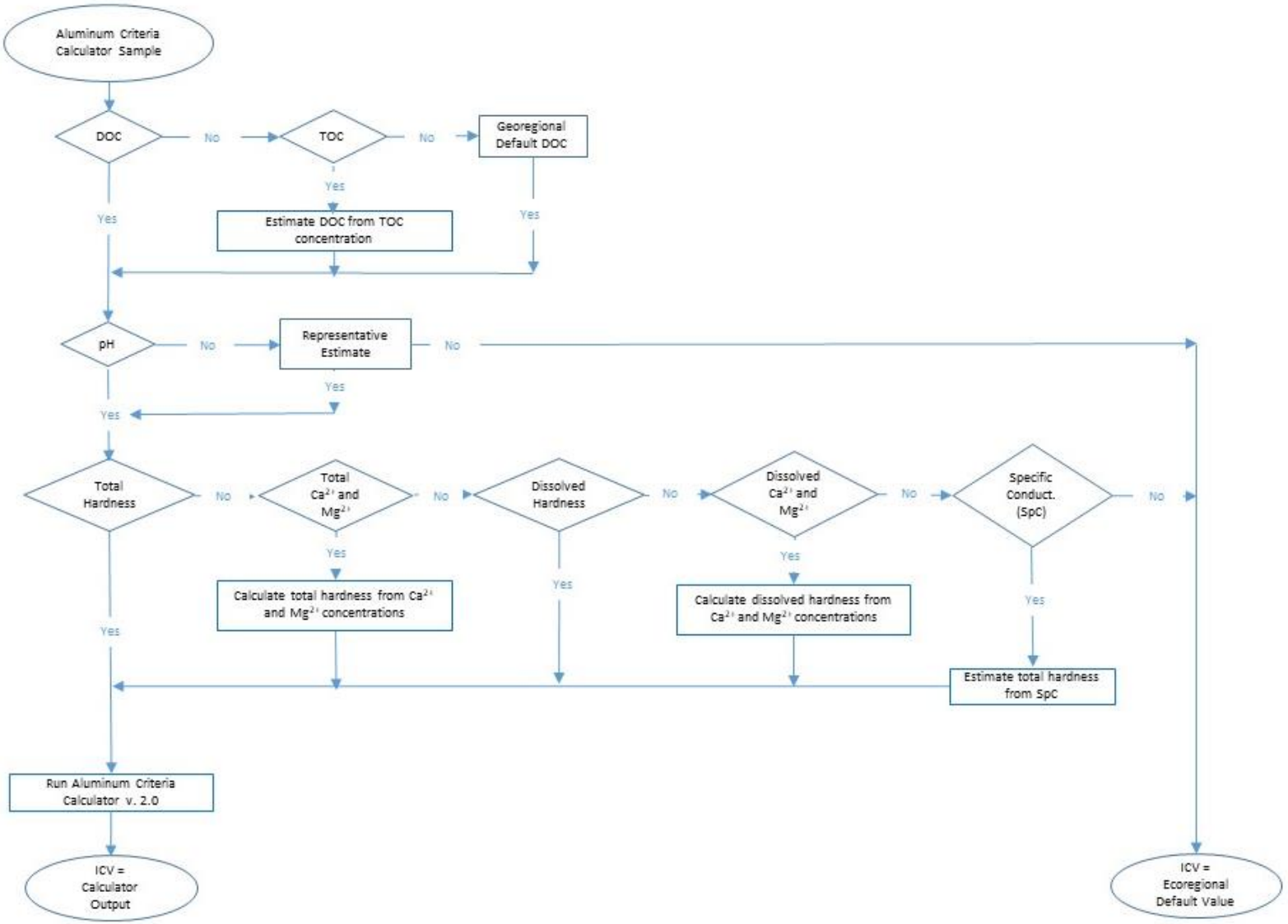
there is sufficient data to derive a representative pH value for the sample and will document the supporting information.

c. If pH has not been measured and a representative pH value cannot be estimated with the available data, the ICV for that sample cannot be calculated. Apply the appropriate **ecoregional default aluminum criterion** provided in Table 2 below.

3. Determine the availability of total hardness measurements.
    a. If total hardness has been measured, enter this value.
    b. If total hardness has not been measured, use the concentration of total Ca^{2+} plus Mg^{2+} ions to calculate the total hardness using **Equation 1** shown below and enter this value.
    c. If total hardness has not been measured, but dissolved hardness has, enter the dissolved hardness value as an estimate of total hardness.
    d. If dissolved hardness has not been measured, use the concentration of dissolved Ca^{2+} plus Mg^{2+} ions to calculate the dissolved hardness using **Equation 1** shown below and enter the dissolved hardness value as an estimate of total hardness.
    e. If neither hardness nor Ca^{2+} and Mg^{2+} have been measured, but specific conductance data is available for the sample, estimate the total hardness concentration using **Equation 2** shown below and enter this value**.**
    f. If specific conductance data are also not available for the sample, and, therefore, total hardness cannot be estimated, apply the appropriate **ecoregional default aluminum criterion** provided in Table 2 below.

4. If sufficient data are available to calculate an ICV, follow the instructions on the "Read Me" tab of the Aluminum Criteria Calculator v 2.0 excel file or the notes within the R Aluminum Criteria Calculator v 2.0 R script (links above) to obtain acute and chronic ICVs for each set of parameter measurements prepared using this procedure. The default input DOC values are available in the next section. If applying a default aluminum criteria value because of insufficient data, those values may also be found in the next section.

Figure 1. Flow Chart for Aluminum Instantaneous Criteria Value (ICV) Calculation



Default georegional DOC input values

Table 1. Default DOC input values for aluminum (June 2021)	
Georegion	**DOC (mg/L)**
Cascades	0.48
Coastal	0.85
Columbia River	1.37
Eastern	0.83
Willamette Valley	0.83

Default georegional DOC input values are based on the following percentiles of the distribution of the available DOC data: 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. Note that these percentiles differ from those used for the copper BLM because of differences in DOC sensitivity between copper and aluminum models. More information about the calculation of default DOC values for aluminum and the georegions can be found in DEQ's *Aluminum Aquatic Life Standard Missing Parameters Document* (ODEQ 2021a). See also the map of the georegions in Figure 2 below.

Equation 1. Calculating hardness from Ca^{2+} and Mg^{2+} concentrations

$$\text{Hardness} = 2.497*[Ca^{2+}] + 4.1189*[Mg^{2+}]$$

If hardness is not directly reported as CaCO3, the above equation (American Public Health Association, American Water Works Association, Water Environment Federation 1998) is used to calculate hardness from the concentration of $Ca^{2+}$and Mg^{2+}, if available. This equation is can be used to calculate total or dissolved hardness, depending on fraction of the input ions. All units are in mg/L.

Equation 2. Estimating total hardness from specific conductance

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

Where, "SpC" is a measurement of specific conductance in µmhos/cm, "ln" is the natural logarithm, and "exp" is a mathematical constant that is the base of the natural logarithm (≈ 2.71828).

Hardness is measured in units of mg/L. More information about the calculation of the relationship between specific conductance and total hardness can be found in DEQ's *Aluminum Aquatic Life Standard Missing Parameters Document* (ODEQ 2021a).

Default ecoregional aluminum criteria values

Table 2. Default aluminum criteria values (June 2021)

Level III Ecoregion	Default Acute Criterion (CMC) µg/L	Default Chronic Criterion (CCC) µg/L
Coast Range	580	300
Klamath Mountains	1500	770
Willamette Valley	830	440
Cascades	360	210
Eastern Cascades Slopes and Foothills	1100	620
Columbia Plateau	1400	800
Blue Mountains	1200	740
Snake River Plain	2900	1200
Northern Basin and Range	1300	680
Columbia River	1600	750

The above ecoregional default aluminum criteria will be applied when either total hardness or pH values are not available and cannot be credibly estimated using the above procedures. In this case, an ICV cannot be derived because there are no default input values for total hardness or pH. Therefore, the default aluminum criteria must be applied until sufficient data are available to derive a sample-specific ICV. For an explanation of why DEQ did not develop default input values for total hardness or pH, please see DEQ's *Aluminum Aquatic Life Standard Missing Parameters Document* (ODEQ 2021a).

The ecoregional default aluminum criteria above are based on the 10^{th} percentile of all ICVs generated from samples with concurrent measured pH and measured or estimated DOC and total hardness measurements from that ecoregion. These default values are inherently conservative to provide protection against potential aluminum toxicity when there is uncertainty due to a lack of input parameter data. DEQ used EPA Level III Ecoregions (EPA 2021b), but calculated a

separate default value for the Columbia River mainstem because it crosses several ecoregions and most of the river flow originates upstream of Oregon (see Figure 3 below). More information about the calculation of default aluminum criteria values can be found in DEQ's *Aluminum Aquatic Life Standard Missing Parameters Document* (ODEQ 2021a).

Figure 2. Georegional Map for Default DOC Input Values

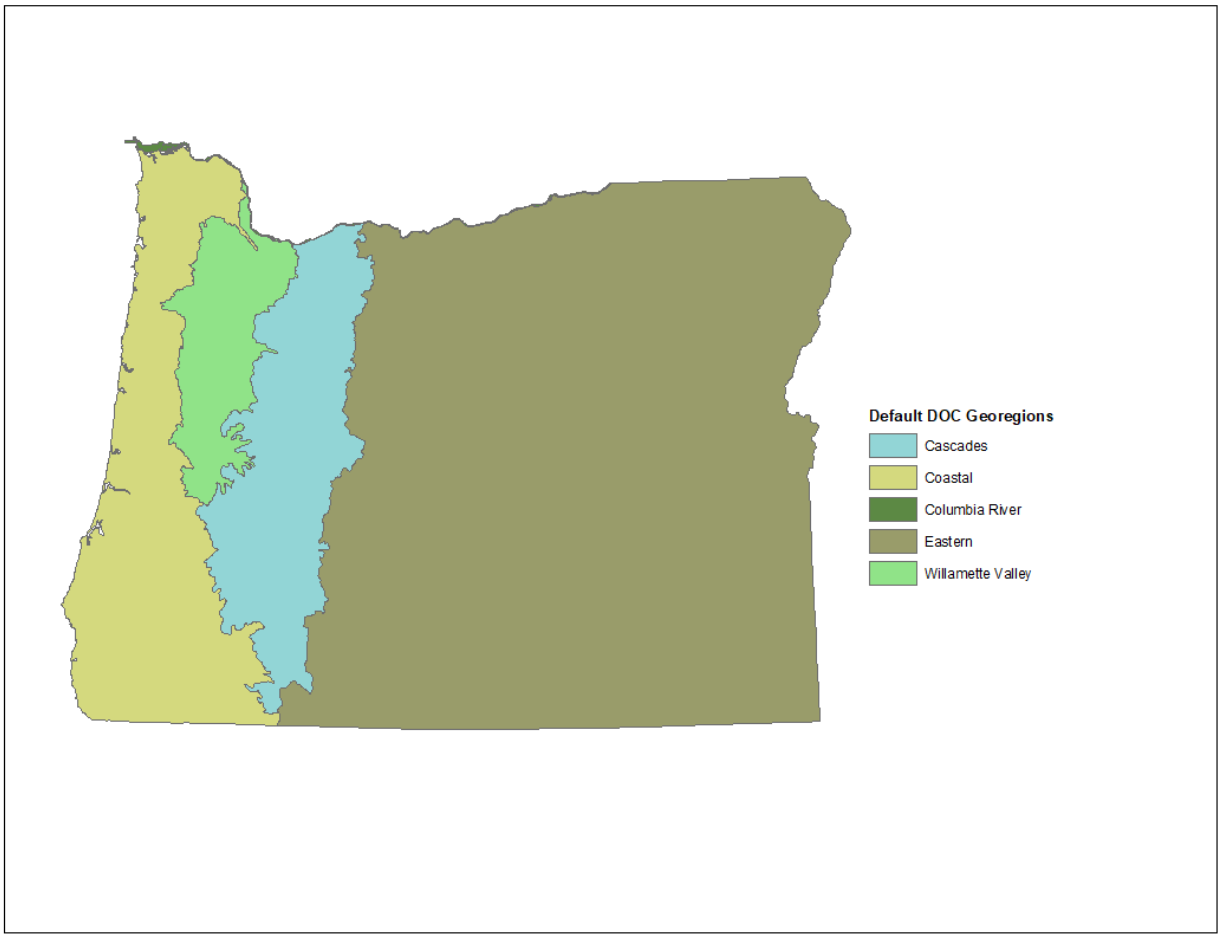
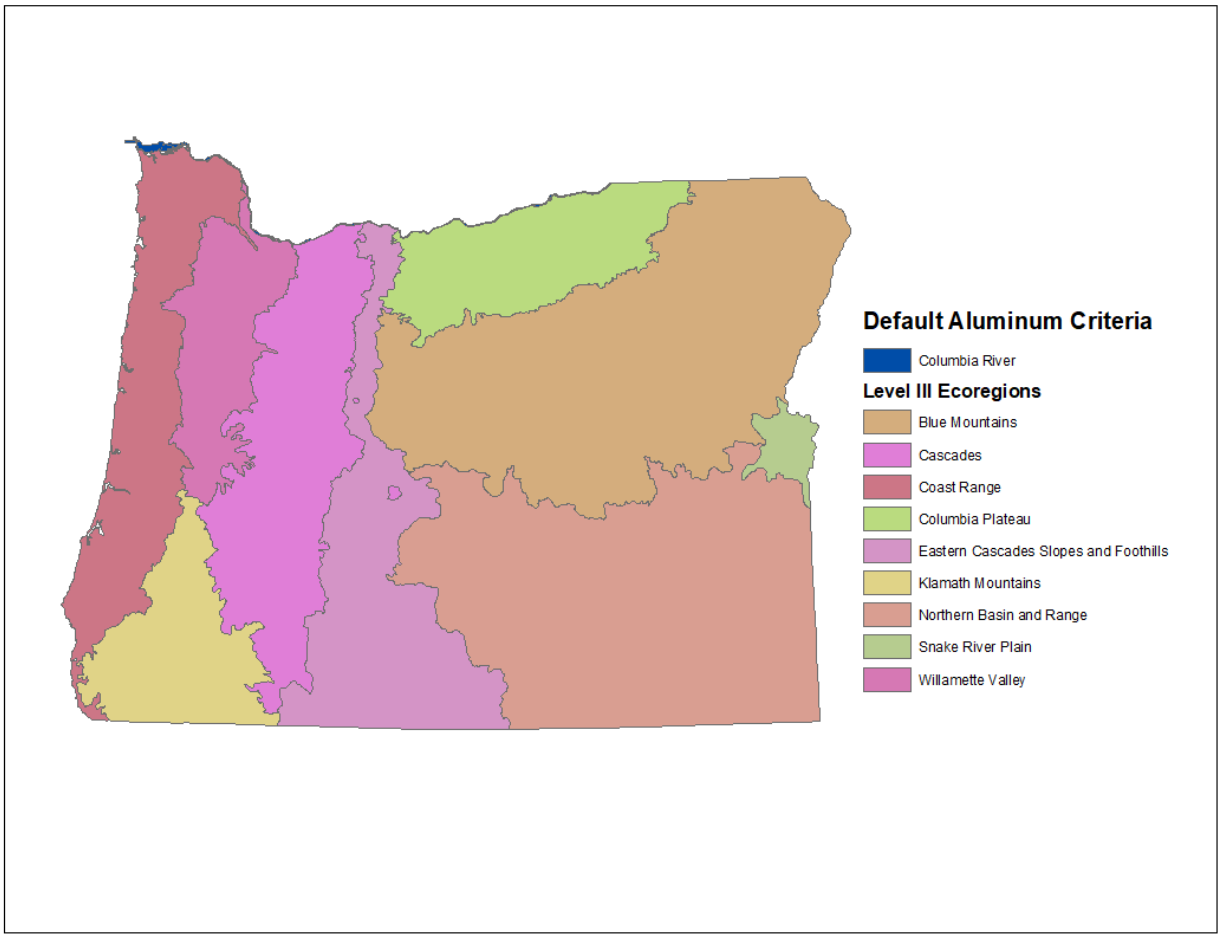


Figure 3. Ecoregional Map for Default Aluminum Criteria Values



References

American Public Health Association, American Water Works Association, Water Environment Federation. 1998. *Standard Methods for the Examination of Water and Wastewater*. 20th ed.

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. 2021a. *Federal Aluminum Aquatic Life Criteria Applicable to Oregon*.

EPA. 2021b. *Level III and IV Ecoregions of the Continental United States*.

ODEQ. 2021a. *Aluminum Aquatic Life Standard Missing Parameters Document*.

ODEQ. 2021b. *Methodology for Oregon's 2022 Water Quality Report and List of Water Quality Limited Waters*.

Rodriguez, PH, JJ Arbildua, G. Villavicencio, P. Urrestarazu, M. Opazo, AS Cardwell, W. Stubblefield, E. Nordheim, and W. Adams. 2019. "Determination of Bioavailable Aluminum in Natural Waters in the Presence of Suspended Solids." 38(8):1668–81.

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] (μg/L)	Criterion continuous concentration (CCC) [4] (μg/L)
Aluminum [1] [2]	7429905	Acute (CMC) and chronic (CCC) freshwater aluminum criteria values for a site shall be calculated using the 2018 Aluminum Criteria Calculator (Aluminum Criteria Calculator V.2.0.xlsx), or a calculator in R or other software package using the same 1985 Guidelines calculation approach and underlying model equations as in the Aluminum Criteria Calculator V.2.0.xlsx, as defined in EPA's Final Aquatic Life Ambient Water Quality Criteria for Aluminum.[5]	

[1]To 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.

[2]These 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.

[3]The 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.

[4]The 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.

[5]EPA–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.