## Rationale for not Adopting EPA's Final Aquatic Life AWQC for Aluminum (2018)

In December 2018, EPA published new ambient water quality criteria for aluminum in fresh water protective of aquatic life. The new criteria structure employs a criteria calculator and requires three input parameters (dissolved organic carbon [DOC], hardness, and pH ) to calculate criteria values for chronic and acute exposure to aluminum. Data are input into the criteria calculator, which uses a multiple linear regression (MLR) model to generate the criteria values for aluminum.

The calculated criteria values are to be compared to data for total recoverable aluminum, even though the current analytical method for total recoverable aluminum measures the sum of both bioavailable and non-bioavailable aluminum, rather than just bioavailable aluminum. This is a significant problem, because any water with suspended aluminosilicate minerals, such as clays, will likely show up as impaired for aluminum when, in fact, the mineral forms of aluminum are not bioavailable at Nevada's ambient values for pH. (The average pH in Nevada's surface waters is 8.2; see Figure 1). This brief paper provides NDEP's rationale for not moving forward to adopt EPA's 2018 criteria for aluminum.

### Toxicity is related to the bioavailability of a chemical

*The toxicity of a chemical to an aquatic organism requires the transfer of the chemical from the external environment to biochemical receptors on or in the organism at which the toxic effects are elicited. Often, this transfer is not simply proportional to the total chemical concentration in the environment, but varies according to attributes of the organism, chemical, and exposure environment so that the chemical is more or less "bioavailable." Definitions of bioavailability vary markedly (e.g., National Research Council, 2003) and are often specific to certain situations, but a useful generic definition is the relative facility with which a chemical is transferred from the environment to a specified location in an organism of interest.* (EPA, 2007)

### Nevada's data for pH, DOC, and hardness

The range of values for each input parameter was evaluated using statewide data for Nevada. These data were compared to the original operating range of the criteria calculator. Data for pH were almost entirely within the original operating range of the model (**Figure 1**). However, for DOC, approximately 25 percent of the statewide data were outside of the original model limits (**Figure 2**). For hardness, approximately 40 percent of the data exceeded the original upper limit of 150 mg/L for the model (**Figure 3**). In the final 2018 criteria document, EPA expanded the ranges of input parameters, stating that "*The bounds for pH of the models ranged from 6.0-8.7. The EPA criteria calculator is designed to allow the user to extrapolate beyond the pH values used to generate the MLR models*."

For DOC, EPA (2018) stated that "*The bounds for DOC of the models ranged from 0.08 to 12.3 mg/L. Since most natural waters contain some DOC, the lower bound of the empirical toxicity test data (0.08 mg/L) is the lowest value that can be entered into the criteria calculator; thus no extrapolation below the lowest empirical DOC of 0.08 mg/L is provided. Similar to hardness, the criteria values generated will be bounded at the upper limit of the empirical MLR models' underlying DOC data, at a maximum 12.0 mg/L DOC in the criteria calculator. The user can input DOC values greater than 12.0 mg/L into the* *calculator, but the criteria magnitude will reach its maximum value at 12.0 mg/L DOC, and criteria magnitudes will not increase or decrease by increasing the DOC above 12.0 mg/L."*

For hardness, EPA stated (2018) that "*The bounds for total hardness of the models ranged from 9.8 to 428 mg/L. Since a decrease in total hardness tends to increase aluminum toxicity, the EPA concludes that it is reasonable to extrapolate below the lower bound of the empirical hardness data of 9.8 mg/L to enable generation of more stringent criteria at low hardnesses. This is consistent with existing EPA approaches to address low end hardness values (U.S. EPA 2002). Therefore, hardness input values in the criteria calculator can be entered that are less than 9.8 mg/L down to a limit of 0.01 mg/L. However, hardness input values into the criteria calculator will be bounded at the approximate upper limit of the empirical MLR models' underlying hardness data, at a maximum of* ***430 mg/L total hardness*** *(as CaCO3)*."

EPA's draft technical support document (TSD) (EPA, 2021) provides the current ranges for input data to the MLR model (**Table 1**). Using these limits, nearly all of Nevada's data for pH and DOC are within range. Hardness, however, remains problematic, with about 15 percent of the data falling above 430 mg/L hardness.

**Table 1. Comparison of MLR models and Criteria Calculator input parameters (EPA, 2021)**

| Input Parameter | MLR Model Range | Criteria Calculator Range |
|---|---|---|
| pH | 6.0 - 8.2 | 5.0 - 10.5 |
| DOC (mg/L) | 0.08 - 12.3 | 0.08 - 12.0 |
| Total hardness (mg/L) | 9.8 - 428 | 0.01 - 430 |

**Figure 1. Statewide data for pH of Nevada's surface waters, compared to original model limits.**

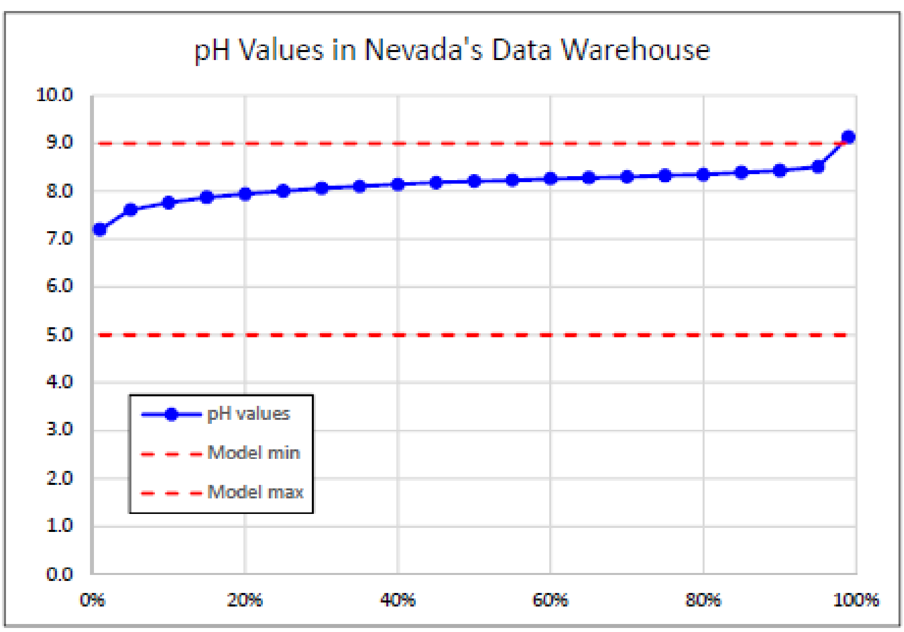


**Figure 2. Statewide data for DOC in Nevada's surface waters, compared to original model limits.**

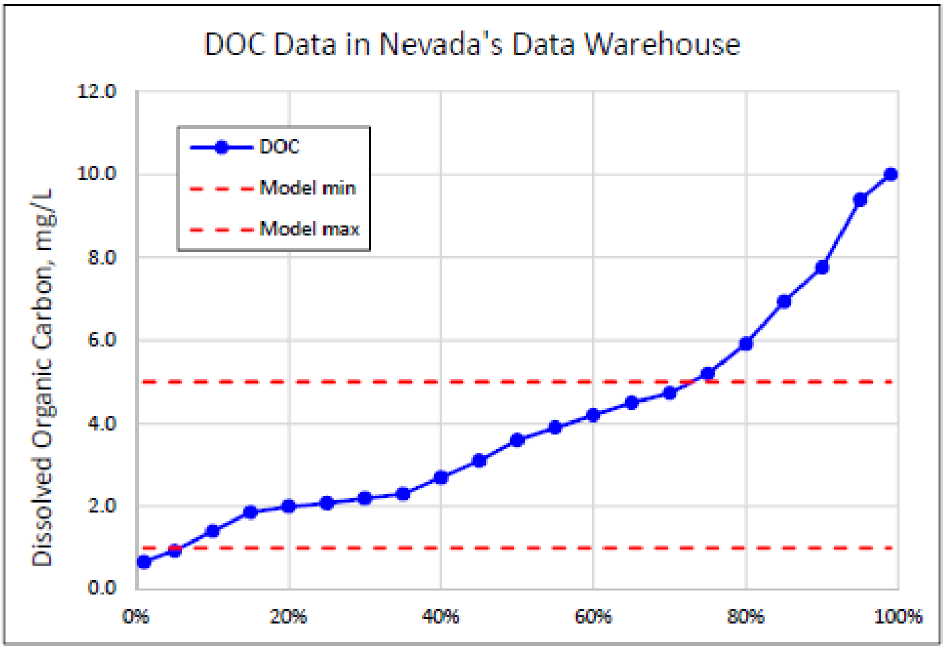
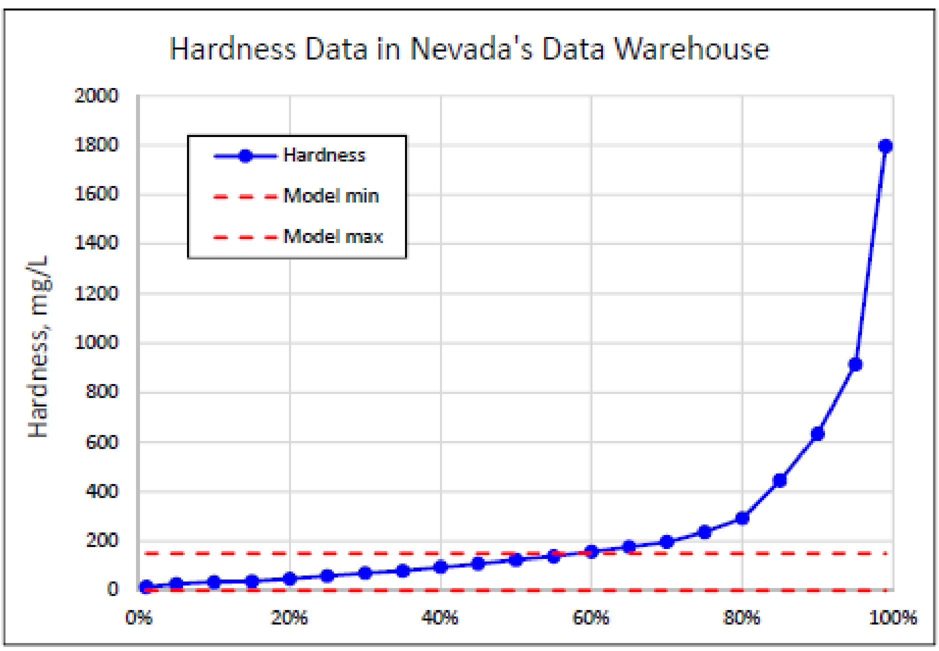



**Figure 3. Statewide data for hardness in Nevada's surface waters, compared to original model limits.**



**EPA's Use of Data for "Total Recoverable Aluminum" for Comparison with Calculated Criteria**

In January 2020, EPA provided responses to the comments received on the *2017 Draft Aluminum Ambient Water Quality Criteria.* There were at least 30 comments on the problem associated with using data for "total recoverable aluminum." Most reviewers (30 of 60) pointed out that the current analytical method, which acidifies the unfiltered sample to pH 1.5, will dissolve suspended clays and other aluminosilicates that are not bioavailable under natural conditions. This will produce numerous false impairments, as clays and other aluminosilicate minerals dissolve in the acidified samples. (Note: kaolinite dissolves congruently at pH 4, thereby releasing all aluminum from the crystal lattice into the acidic solution). This issue makes adoption of the current criteria untenable for Nevada.

> ***EPA responded to the 30 comments regarding dissolution of clays, stating that:***
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> "*The EPA is aware, and has noted in the 2018 aluminum criteria document, that under natural conditions not all forms of aluminum would be biologically available to aquatic species (e.g., clay-bound aluminum). The EPA has also noted in its 2018 final aluminum criteria document that the EPA Methods 200.7 and 200.8 are the only currently approved methods for measuring aluminum in natural waters and wastes for NPDES permits. The EPA further notes that research on new analytical methods is ongoing to address concerns with including* ***aluminum bound to particulate matter (i.e., clay)*** *in the total recoverable aluminum concentrations (OSU 2018c).*
>
> *The 1988 AWQC for aluminum were discussed as acid-soluble concentrations and were subsequently expressed in terms of total recoverable aluminum. Dissolved, colloidal and precipitated forms of aluminum are all bioavailable to aquatic organisms, which supports the criteria as total aluminum. Thus, if aluminum criteria are based on dissolved concentrations, toxicity would likely be underestimated, as colloidal forms and hydroxide precipitates of the metal that can dissolve under natural conditions and become biologically available would not be measured.*
>
> *The current EPA approved CWA Test Method (Methods 200.7 and 200.8) for aluminum in water and wastes by inductively coupled plasma-atomic emission spectrometry and inductively-coupled plasma-mass spectrometry measures total recoverable aluminum (U.S. EPA 1994a,b). This method is based on acid soluble aluminum where the sample is acidified to pH<2 and then filtered through a 0.45 µm filter.* ***This process does dissolve*** *the monomeric and polymeric forms of aluminum,* ***in addition to colloidal, particulate, and clay aluminum****. However, the EPA Methods 200.7 and 200.8 are the currently approved methods for aluminum.*
>
> *In the 2018 Final aluminum criteria document the EPA has noted that external research on new analytical methods is ongoing to address concerns* ***with aluminum bound to particulate matter (i.e., clay)[1] from natural waters*** *being included in the total recoverable aluminum concentrations.*

[1] NOTE: Aluminum is not "bound to clay;" rather, the aluminum atom is an integral part of the crystal lattice in clays and other aluminosilicate minerals. This is a big difference, and it suggests that EPA does not understand the extent of the problem created by requiring use of data for "total recoverable aluminum."

*This approach would not acidify the sample to pH<2 but rather to a higher pH to better capture the bioavailable fraction of aluminum. The method has recently been published as Rodriguez, P.H., J.J. Arbildua, G. Villavicencio, P. Urrestarazu, M. Opazo, A.S. Cardwell, W. Stubblefield, E. Nordheim, and W. Adams. 2019. Determination of Bioavailable Aluminum in Natural Waters in the Presence of Suspended Solids. Environ. Toxicol. Chem. 29 April 2019. https://doi.org/10.1002/etc.4448. The expectation is that this approach may better estimate the bioavailable fraction of aluminum in natural waters."*

## An Overview of Nevada's Data Run Through the Criteria Calculator

In 2020, NDEP ran a number of data scenarios through the Criteria Calculator to test model limits. The minimum and maximum values triggered a warning of "Outside model inputs," which is not unexpected. However, using median values for all inputs also triggered this message (**Table 2**).

**Table 2. Summary Statistics for Nevada Data (11-13-20) and Input into the Aluminum Criteria Calculator**

| NV statistic | DOC (mg/L) | Total Hardness (mg/L as $CaCO_3$) | pH | CMC | CCC | Flag |
|---|---|---|---|---|---|---|
| Min model | 0.1 | 0.8 | 5 | 0.083 | 0.052 | Outside model inputs |
| Max model | 12.0 | 430 | 10.5 | 200 | 120 | Outside model inputs |
| Min NV, avg pH | 0.3 | 0.8 | 8.15 | 350 | 220 | |
| Max NV, avg pH | 12.0 | 430 | 8.15 | 4700 | 1000 | |
| Min NV, min pH | 0.3 | 0.8 | 5 | 0.18 | 0.11 | Outside model inputs |
| Max NV, max pH | 12.0 | 430 | 10.5 | 200 | 120 | Outside model inputs |
| Avg NV all means | 3.6 | 248 | 8.15 | 3300 | 1200 | |
| **Avg NV all medians** | **2.7** | **124** | **8.21** | 3100 | 1400 | **Outside model inputs** |
| Max DOC, Avg pH, Max H | 12.0 | 430 | 8.15 | 4700 | 1000 | |
| Max DOC, Avg pH, Avg H | 12.0 | 248 | 8.15 | 4700 | 1100 | |
| Max DOC NV, min pH | 12.0 | 430 | 5 | 600 | 380 | Outside model inputs |
| Min DOC , min pH, med hard | 0.3 | 124 | 5 | 21 | 13 | Outside model inputs |
| Min DOC , max pH, med hard | 0.3 | 124 | 10.5 | 33 | 20 | Outside model inputs |

## Nevada's Conclusion Regarding EPA's 2018 Aluminum Criteria

EPA's draft TSD states that "*EPA expects that an adjusted analytical method (referred to as a bioavailable analytical method) that uses a less aggressive initial acid digestion that liberates bioavailable forms of aluminum (including amorphous aluminum hydroxide) yet that minimizes dissolution of mineralized forms of aluminum (such as aluminosilicate minerals associated with suspended sediment particles) will better estimate the bioavailable fraction of aluminum under natural instream conditions*." Until such time that such a bioavailable method is developed and approved by EPA, and sufficient time passes to collect aluminum data using this method, Nevada will focus on adopting water quality standards other than aluminum. Nevada believes that EPA should have anticipated the problem with dissolution of suspended aluminosilicate minerals, and developed and approved a "bioavailable" analytical method prior to publishing the new criteria for aluminum.

## References

EPA, 2007. Aquatic Life Ambient Freshwater Quality Criteria – Copper. EPA-822-R-07-001. February. https://www.epa.gov/sites/default/files/2019-02/documents/al-freshwater-copper-2007-revision.pdf

EPA, 2018. Final Aquatic Life Criteria for Aluminum in Freshwater. EPA-822-R-18-001. December. https://www.epa.gov/wqc/2018-final-aquatic-life-criteria-aluminum-freshwater