2022 Integrated Report Assessment Methodology

Draft: Continuous pH Methodology Development

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

Introduction and background

The pH of water, commonly understood as acidity or alkalinity, is a measure of the hydrogen or hydronium ions concentration. It is reported on a logarithmic scale where values under 7 represent acidic waters and values above 7 represent alkaline waters. Chemical and biological processes in natural waterbodies are influenced by the pH of the water. It is one of the most important environmental factors limiting species distributions in aquatic habitats. The pH of water determines the solubility (amount that can be dissolved in the water) and biological availability (amount that can be utilized by aquatic life) of chemical constituents such as nutrients (phosphorus, nitrogen, and carbon) and heavy metals (lead, copper, cadmium, etc.). The toxicity of many compounds is affected by the degree of dissociation. Several recent examples of toxics criteria dependent at least partially on pH are ammonium, copper criteria using the biotic ligand model, and EPA's recently promulgated aluminum criteria.

The photosynthetic activity of aquatic plants and algae impacts the concentrations of dissolved oxygen, dissolved carbon dioxide and pH through the course of a day. This diurnal pattern results in higher pH values in the afternoon when carbon dioxide consumption and dissolved oxygen respiration is the greatest. At night when this process shifts to respiration, pH values drop and the waterbody becomes more acidic (Figure 1). The range of these diurnal patterns vary naturally across the diverse ecosystems of Oregon, and can also be magnified as a result of human activity. For those parameters that exhibit significant diurnal fluctuations and/or natural variability, interpreting what constitutes an "impairment" can be problematic. Oregon's current pH criteria were developed when the availability of continuous data for assessment purposes was cost prohibitive and time consuming. With the continued advancement in continuous data collection technology, large quantities of time series (continuous) data are now being collected routinely for dissolved oxygen (DO), temperature, and pH. The intent of this paper is to introduce a new method for utilizing continuous pH in the 2022 Integrated Report (IR). Of primary concern are evaluating appropriate duration and frequency components of the pH standard – how long and how often excursions outside the criteria range can occur before there is an adverse impact on aquatic life, because the environment fluctuates due to both natural variability and human activity,. The method will also address the rapid changes in pH outside the criteria range that are shown to have an impact on fish and aquatic life.

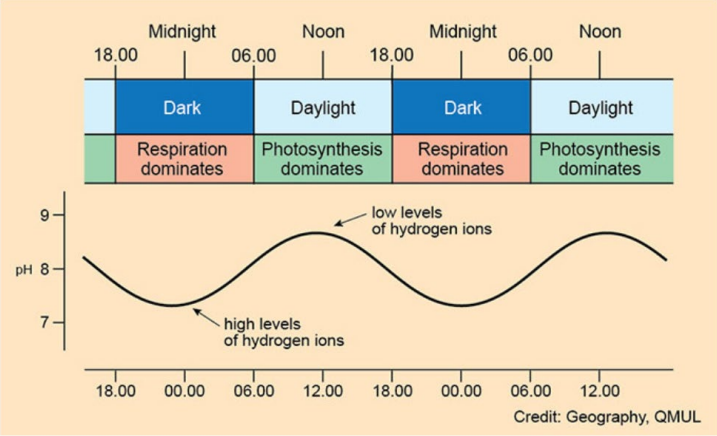


Figure 1. Daily fluctuations in pH as a result of photosynthesis. Car
/www.qmul.ac.uk/chesswatch/water-quality-sensors/ph/

Basis for Oregon's pH Standard

The pH water quality standard was developed to protect the most sensitive beneficial use. For pH, this was determined to be the fish and aquatic life use, specifically salmonids and resident fish. The first numeric criteria for pH in Oregon were promulgated from the U.S. EPA 1986 quality criteria for water ("Gold Book") (EPA 1986). Oregon evaluated pH criteria as part of a triennial review in 1995, and adopted basin-specific pH criteria that range from 6.0 – 9.5 pH units in 1996. Oregon's criteria included adjustments to the recommended national criteria to account for natural conditions in certain regions of the state. Oregon's current criteria range accounts for the natural variation in Oregon streams from

rainwater dominated coastal and Cascade basins to alkaline conditions that dominate arid interior basins. The current pH criterion is defined by OAR 340-041-0021(1) (see below).

"*Unless otherwise specified in OAR 340-041-0101 through 340-041-0350, pH values (Hydrogen ion concentrations) may not fall outside the following ranges: (a) Marine waters: 7.0-8.5; or (b) Estuarine and fresh waters: See basin specific criteria (OAR 340-041-0101 through 340-041-0350)*."

The 1995 triennial review issue paper also recognized the effects of rapid changes in magnitude on the most sensitive beneficial use, salmonids and resident fish (Oregon DEQ 1995). Studies on invertebrates and salmonids noted that rapid changes in pH within the recommended criteria range were not observed to be detrimental to aquatic life. Both rainbow trout and benthic invertebrates were observed to adapt rapidly to "shock" changes within this range. However, rapid shifts small as +/- 0.5 pH units outside of this range were shown to be harmful to rainbow trout if they occurred quickly, on the scale of minutes, but were better tolerated if they occurred gradually over the scale of days (Road and Grove 2004).

pH and the Integrated Report

The Clean Water Act section 303(d) requires states to identify waters not meeting water quality criteria. The 303(d) list of impaired waters is one component of the Integrated Report requirement. DEQ has assessed pH data for the report since 1986. The current assessment methodology is based on grab sample data. Waterbodies are considered to be impaired when greater than 10% of the samples fall outside the range of the appropriate criterion according to the exact binomial test, with a minimum of five samples.

Given that limited time series pH data was available in the evaluation of pH standards during the 1995 triennial review, the integrated report methodology must define what constitutes an exceedance under the standard in continuously monitored datasets and provide a means to evaluate them that is consistent with evaluation of more traditional grab sample datasets. Due to inherent serial correlation of time series data, evaluation of averages or counts of individual measurements in continuous datasets as if they were instantaneous samples is not appropriate

Binomial Statistical Test Method

For the 2018/2020 Integrated Report, DEQ adopted the exact binomial test as a statistical method for categorical assignment (Category 5 = Impaired and Category 2 = Attaining). This statistical method culminates in a table which scales the percent exceedance rate with the sample size based on the desired confidence interval. Figure 2 shows the binomial test parameters and critical exceedance values as defined in ***Methodology for Oregon's 2018 Water Quality Report and List of Water Quality Limited Waters.***

Critical Values for Listing Conventional Pollutants[20]

Null Hypothesis: Actual exceedance proportion is ≤10%
Alternate hypothesis: Actual exceedance proportion is >10%
Minimum confidence level is 90%
A minimum sample size of five is required.

Table 6. Minimum number of sample excursions required to list as impaired for conventional pollutants

Sample Size	List if excursions ≥ :
5 - 11	2*
12-18	4
19-25	5
26-32	6
33-40	7
41-47	8
48-55	9
56-63	10
64-71	11
72-79	12
80-88	13
89-96	14
97-104	15
105-113	16
114-121	17
122-130	18
131-138	19

[20] Excluding continuous dissolved oxygen and temperature

Figure 2.The binomial test parameters and critical exceedance values as defined in Methodology for Oregon's 2018 Water Quality Report and List of Water Quality Limited Waters

Review of methods used by other states

DEQ reviewed the methods other states use to assess continuous data. Figure 3. Summarizes methods other states use to assess continuous data for their Integrated Reports.

Table 1. Methods used by states to assess continuous data.

State	Assessment	Data used in calculation
Arkansas	> 10% exceedances using the binomial	Long-term continuous data taken in less than hourly readings (example: data recorded every fifteen minutes) will be averaged into an hourly average reading
California	Exceed minimum or maximum daily value by > 10% using binomial	
Missouri	Data collected in a time series fashion will be looked at on a 4 day period. If an entire 4 day period is outside of the 6.5 - 9.0 criterion range that will count as a chronic toxicity event. More than one of these events will constitute an impairment listing of the stream.	Continuous data
Nevada	> 10% exceedance of WQS	Daily min/max values calculated from continuous datasets
New Mexico	Any one of the following: 1) >10% exceedance of WQS based upon all data	Continuous Data
	2) Any exceedances occur for more than 24 consecutive hours	
	3) pH exceeds 9.5 at any time	
New Jersey	1 exceedance of WQS at least 1 hour duration	All continuous data
Virginia	> 10.5% of readings in a 24-hour period exceed WQS	A day violates WQS when > 10.5% of readings violate WQS
Washington	Hypergeometric test (exceedance rate = 5%) is failed in one or more calendar years based on time series data	All continuous data
Wisconsin	> 10% exceedance of WQS	All continuous data

Most states use one of the options summarized below:

Evaluation of chronic pH

Data collected in a time series fashion are evaluated using a 4-day chronic statistic. If an entire 4-day period is outside of that state's 6.5 - 9.0 criterion range that constitutes a chronic toxicity event. Where greater than 10% of the chronic toxicity events falls outside the range of the appropriate criterion according to the exact binomial test, the waterbody would be considered impaired.

Daily Min/Max - Binomial 10%

Data collected in a time series fashion are evaluated using daily minimum and maximum statistics. Each daily value constitutes one sample. Where greater than 10% of the daily min/max values falls outside the range of the appropriate criterion according to the exact binomial test, the waterbody would be considered impaired.

10% - 10% rule

Data collected in a time series fashion are evaluated using a daily statistic. A day is considered in violation of its WQS when > 10% of readings fall outside the specified pH range. Where greater than 10% of the daily values falls outside the range of the appropriate criterion according to the exact binomial test, the waterbody would be considered impaired.

Exploring the Options

DEQ explored using the Daily Min/Max - Binomial 10% and the 10%-10% rule using a dataset and binomial test parameters consistent with the 2018/2020 IR data window. The chronic method was not evaluated as DEQ staff believe this was not the intent of its numeric criteria. Figure 3. Flow charts showing the daily min/max binomial 10% compared to the 10-10% rule; methods DEQ evaluated for the proposed continuous pH method.

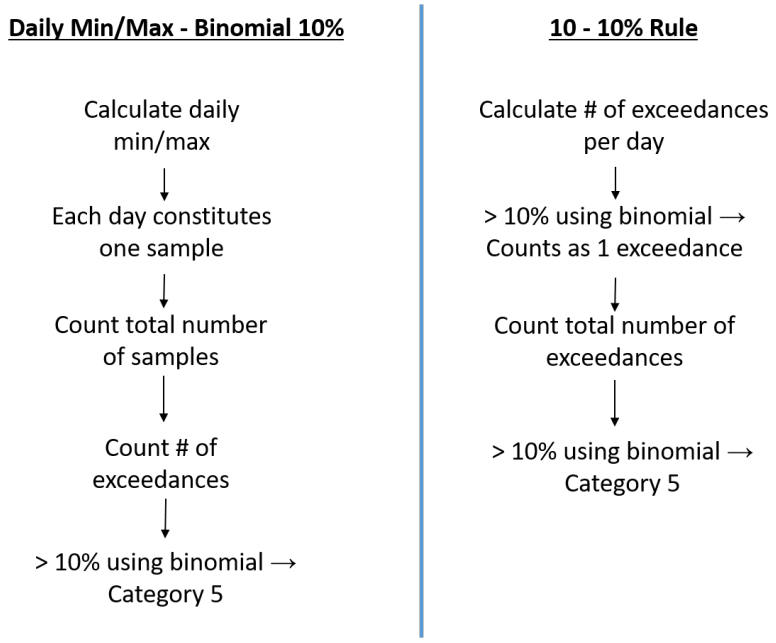


Figure 3. Daily min/max binomial 10% compared to the 10-10% rule

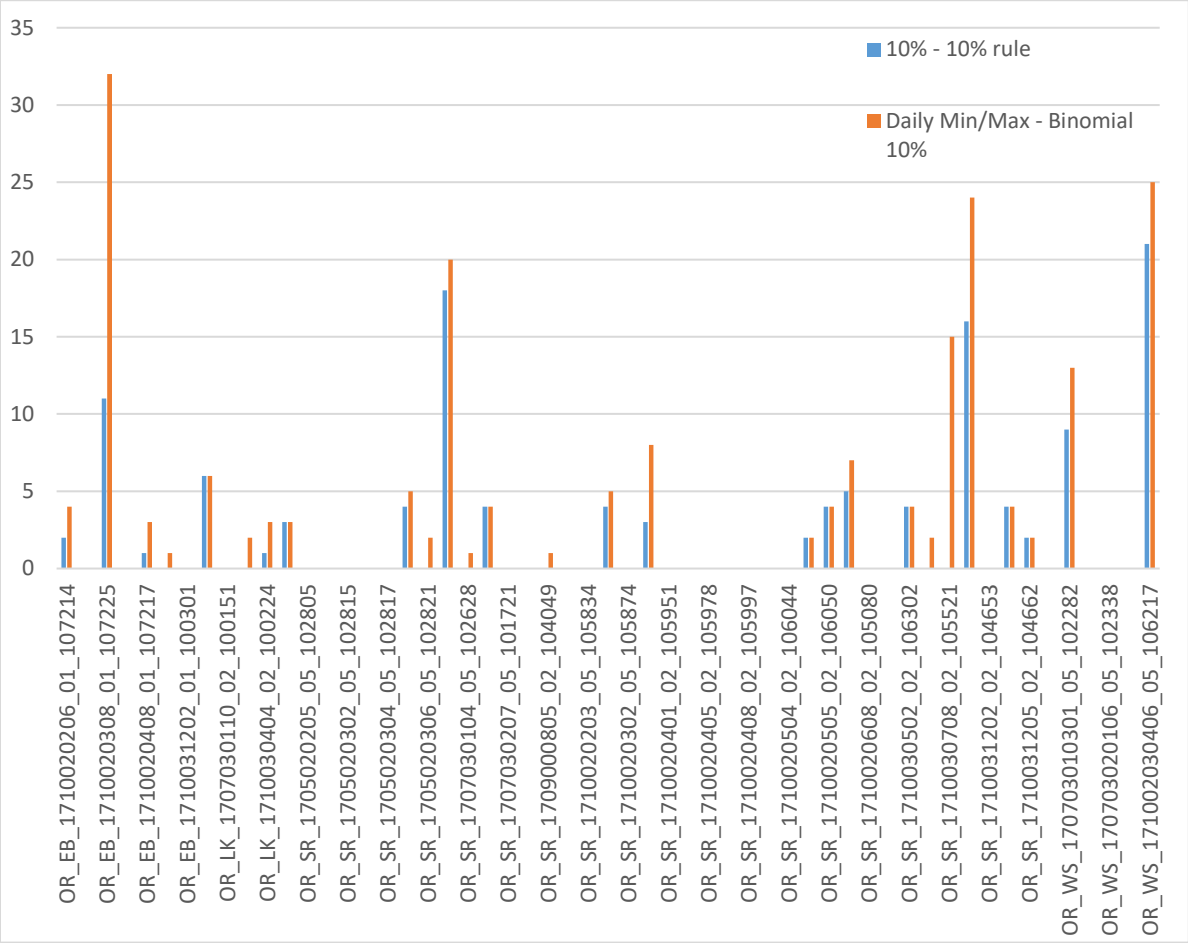


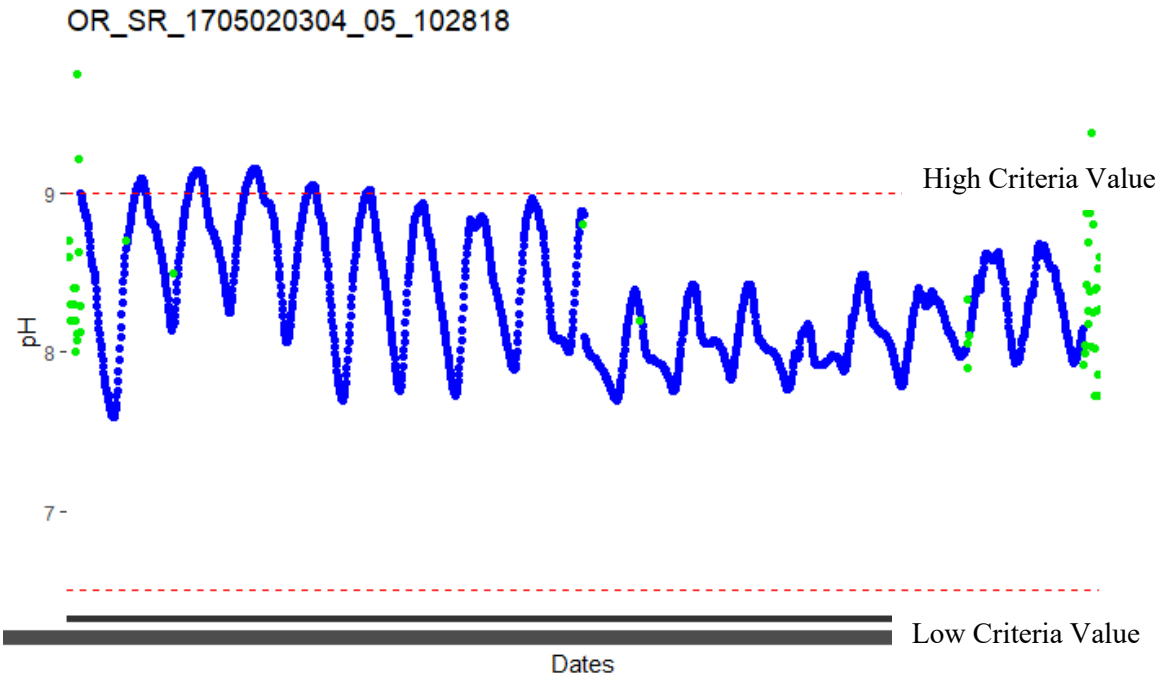
Figure 4. Side by side comparison of the total number of exceedances when using the different methods on the same dataset.

Recommended Methodology for Continuous pH data

Based on the data exploration, DEQ is proposing to use the 10%-10% rule to assess continuous pH data for the Integrated Report. This recommendation is based on balancing the diurnal swings in pH with the intent of the Water Quality Standard. Counting an exceedance based solely on a minimum or maximum daily value may lead to a higher rate of inappropriate pH listings because it would only be assessing the extremes and not evaluating the entire diurnal cycle. For many assessment units, DEQ will likely continue to have a combination of continuous and grab pH data. For this reason the proposed method for combining continuous and grab data within an assessment unit is summarized below. When only grab data is available, DEQ will continue to use the grab data method outlined in the *Methodology for Oregon's 2018 Water Quality Report and List of Water Quality Limited Waters.*

- Greater than 10% of the daily time-series measurements are outside the range of the appropriate criterion according to the exact binomial test is equivalent to a daily exceedance of the criterion.
- Tally the number of exceedances of grab data results
- Confirm that there are not exceedances for the same location and day for grab and continuous results

- Sum the number of grab samples and sample days from continuous results
- Sum the number of daily exceedances and the number of grab sample exceedances
- Plug into the exact binomial with the same critical values for listing conventional pollutants (i.e. Null Hypothesis: Actual exceedance proportion is ≤10%) to determine the critical value of exceedances and the final IR category



Method	Number days/ Number samples	Exceedances	List if Exceedances ≥	IR Category
(Blue) 10% - 10% rule	21	4	5	Cat2
(Green) Grab Only	56	6	10	Cat2
Combined	**77**	**10**	**12***	**Cat2**

*(critical value for 77 samples)

Figure 5. Proposed method combining continuous pH data with grab pH data at the Assessment Unit scale

Additionally, to address concerns raised in the 1995 issue paper, DEQ will assess continuous pH data to detect rapid changes either above or below the basin specific numeric criteria range. Any waterbody with two or more 24-hour periods with a change of +/- 0.5 pH units outside of the numeric criteria range will be classified as impaired (Category 5).

Delisting

Waters will be removed from the section 303(d) list of impaired waters if the number of exceedances of the numeric criterion supports the rejection of the null hypothesis of the binomial test. DEQ is proposing to continue to use the binomial method to delist for pH using the same method to combine grab and continuous datasets and applying the critical values for delisting outlined in Figure 6. DEQ believes this method is a valid approach for delisting based on continuous data for parameters that do not specify summary statistics as part of their numeric criteria (i.e. dissolved oxygen). Figure 6 shows DEQ's confidence level and critical values for the binomial statistical test for delisting conventional pollutants.

Critical Values for Delisting Conventional Pollutants

Null Hypothesis: Actual exceedance proportion is >10%
Alternate hypothesis: Actual exceedance proportion is ≤10%
Minimum confidence level is 90%
A minimum sample size of 15 is required.

Table 10. Maximum number of sample excursions to delist as impaired for conventional pollutants

Sample Size	Delist if excursions ≤ :
15	1
16-18	2
19-25	3
26-32	4
33-40	5
41-47	6
48-55	7
56-63	8
64-71	9
72-79	10
80-88	11
89-96	12
97-104	13
105-113	14
114-121	15
122-130	16
131-138	17
139-147	18

Figure 6. Figure 6 DEQ's confidence level and critical values for the binomial statistical test for delisting conventional pollutants

Conclusion

Due to the increasing use of sensors which can collect reliable, high quality water quality data, DEQ sought to develop a method to utilize this data stream in the Integrated Report. DEQ conducted a review of methods used by other states and explored options considered to be consistent with the intent of WQS using Oregon data. From this analysis, DEQ is recommending using the 10%-10% rule to assess continuous pH data for the IR. This method utilizes the exact binomial twice, once to determine the occurrence of a daily exceedance and again to determine a final conclusion for the entire range of the data (can be a combination of grab and continuous) available for a particular assessment unit.

The DEQ 1995 issue paper, written at a time when limited diurnal (continuous) data was available, expressed concern that statistical analysis of large amounts of data collected consistently over regular diurnal patterns can lead to biases. At that time it was anticipated that a summary statistic of a daily minimum or maximum would better represent the data. This recent analysis indicates that when using

continuous data to determining compliance of numeric criteria, applying the exact binomial test with a greater than ten percent exceedance rate on a daily basis can better represent diurnal datasets than only evaluating daily maximums or minimums.

References

EPA 1986 – USEPA Quality Criteria for Water 1986. https://www.epa.gov/sites/production/files/2018-10/documents/quality-criteria-water-1986.pdf

Oregon DEQ 1995 – Final Issue Paper – pH Hydrogen Ion Concentration 1992-1994 Water Quality Standards Review.

Road, W., and E. Grove. 2004. pH Requirements of Freshwater Aquatic Life. Technical Memorandum, Robertson-Bryan Inc., Central Valley California Water Resources Control Board.

Oregon DEQ 2018 - *Methodology for Oregon's 2018 Water Quality Report and List of Water Quality Limited Waters. https://www.oregon.gov/deq/wq/Documents/irMethodologyF1820.pdf*