pH Assessment Method for Streams and Rivers in Montana

Public Comment Draft, November 2025
Document ID provided when finalized, Version 1.0

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Document Revision and Version History

Revision Date	Version number	Summary of change(s)	Revised sections(s)	Revised by
November 2025	1.0	Initial document	All	Blake Towarnicki

Suggested Citation

Montana Department of Environmental Quality, 2025. *pH Assessment Method for Streams and Rivers in Montana*. Document ID, Version 1.0. Montana Department of Environmental Quality: Helena, Montana.

TABLE OF CONTENTS

LIST OF TABLES

ACRONYMS

AMD	acid mine drainage
ARM	Administrative Rules of Montana
AU	assessment unit
CFR	Code of Federal Regulations
DEQ	Montana Department of Environmental Quality
DQA	data quality assessment
EPA	US Environmental Protection Agency
MCA	Montana Code Annotated
mol/L	moles per liter
pH	potential of hydrogen
QA	quality assurance
QC	quality control
SOP	standard operating procedure
TMDL	total maximum daily load
WARD	Water Quality Assessment and Reporting Documentation
WQPB	Water Quality Planning Bureau
WQS	water quality standards

CHEMICAL FORMULAS

CO_2	Carbon Dioxide
H^+	Hydrogen Ion
H_2O	Water

1.0 INTRODUCTION

This document details the Montana Department of Environmental Quality's (DEQ) potential of hydrogen (pH) assessment method for streams and rivers. This method will be used as guidance to assess the aquatic life beneficial use for all water classifications. The Beneficial Use Assessment for Montana's surface waters describe the overall process to complete a beneficial use assessment for a waterbody (Makarowski 2020). Aquatic life is the beneficial use most sensitive to impairments caused by fluctuations in pH. However, other beneficial uses may be impacted during extreme changes. This assessment method is not a state rule or regulation.

1.1 APPLICABILITY

This assessment method provides guidance for, and is applicable to, all streams and rivers under Montana state authority. State surface waters are classified in accordance with their present and future beneficial uses per the Montana Water Quality Act (75-5-301[1], Montana Code Annotated [MCA]).

1.2 BACKGROUND INFORMATION

pH is a measure of the hydrogen (H^+) concentration in water. Specifically, pH is the negative logarithm of hydrogen ion concentration (mol/L) in an aqueous solution: pH = $-\log_{10}(H^+)$ (EPA 2023). The term pH is commonly used to indicate the change in basicity or acidity of a solution. pH is typically shown ranging from 0 to 14, with 7 considered neutral. The acidity of a solution increases with higher concentrations of H^+, corresponding to lower pH. Conversely, lower concentrations of H^+ in solution occur in a more basic solutions, resulting in higher pH values.

pH is an important factor in the chemical and biological systems of natural waters that can limit the distribution of aquatic species. It can exert direct toxicity by affecting cell membrane processes, gill function, and other physiological stress to aquatic organisms. Additionally, pH influences the toxicity of many compounds, solubility of metals, and bioavailability of nutrients, and for this reason it is considered a master variable in aqueous chemistry and toxicology (EPA 1986).

1.3 DRIVERS OF PH VARIABILITY

Normal conditions in rivers and streams exhibit a diurnal cycle of pH variations due to the processes of photosynthesis and respiration by algae and plants. Daily shifts are intensified during the growing season (i.e., summer and fall when algae and plants are abundant and photosynthetically active) because of increased light, temperature, and nutrient availability in the water column.

Typically, early mornings show the lowest pH levels because of increased carbon dioxide (CO_2) in the system from respiration of aquatic plants and other aquatic organisms, and minimal plant photosynthesis. Late afternoons commonly exhibit higher pH levels due to aquatic plants using up the available CO_2 for photosynthesis, shifting the chemical equilibrium towards greater bicarbonate and carbonate concentrations, and thus higher pH values.

Additionally, exposure of sulfur bearing minerals from mining and other chemical interactions from industrial point sources may affect pH. Some point sources have the potential to shift pH if treatment is not adequate.

1.3.1 Eutrophication

Eutrophication is the enrichment of a waterbody by nutrients (nitrogen and phosphorus), leading to increased plant and algae growth and decay, and secondary effects to water quality that occur because of this enrichment. Common sources of nutrients include fertilizer runoff from agriculture, poorly managed grazing, municipal wastewater effluent, mining operations, and home septic systems.

1.3.2 Acid Mine Drainage

Acid mine drainage (AMD) refers to the outflow of acidic water from some metal or coal mines. The site-specific geology and mineralogy, mining methods, and materials management are primary factors that influence the potential occurrence of AMD. This acidic water is often rich in dissolved metals which are leached out from rocks and ores exposed during mining activities. When certain sulfur-bearing minerals in the mined rock are exposed to oxygen and water, they can react to form acids which can significantly lower the pH of water. The pH of AMD is usually in the range of 2 to 6, but not all mine-impacted waters are overly acidic. A similar process known as “acid rock drainage” may occur naturally, in the absence of mining, if certain sulfur-bearing minerals are present and become reactive from exposure to oxygen and surface water or groundwater.

1.4 Potential Sources

Probable sources of impairment are the activities, facilities, or conditions that generate pollutants that prevent waterbodies from meeting water quality standards. The following sources are most commonly associated with pH impairment listings in Montana:

- Mining/Abandoned Mine Lands
- Industrial and Municipal Point Source Discharge
- Accidental Release/Spills
- Agriculture and Livestock
- Natural Sources
- Dam or Impoundment
- Loss of Riparian Habitat
- On-site Treatment Systems (Septic Systems and Similar Decentralized Systems)
- Urban Runoff/Storm Sewers
- Erosion and Sedimentation

Best professional judgment should be used to determine any other significant sources on a site-by-site basis. For many of the streams in Montana, pH is related to and addressed by metals and nutrient assessments and total maximum daily loads (TMDL). Human influences of altered pH may be controlled through best management practices or remediation activities that reduce nutrients or AMD.

1.5 Impacts on Beneficial Uses

Both high and low pH values in a waterbody can negatively impact the growth and propagation of aquatic life by exposing fish and aquatic macroinvertebrates to excess or diminished concentrations of H^+. These altered concentrations can affect their cellular osmoregulation and enzyme activities within their bodies. When the pH of freshwater becomes highly basic or acidic, the effects on fish may include:

- Mucus on gills
- Decreased growth
- Reproductive failure

- Respiratory inhibition
- Ionoregulatory impacts
- Reduced number of sensitive species and individuals
- Mortality
- Decreased reproduction
- Reduced biodiversity
- Damage to skin, gills, olfactory organs, eyes (EPA 2023)

2.0 WATER QUALITY STANDARDS

Montana water quality standards (WQS) designate the allowable concentration of pollutants, or the condition of a waterbody that will protect the beneficial uses. Beneficial uses and water quality criteria provide the framework for achieving federal Clean Water Act (40 Code of Federal Regulations [CFR] 131.2) and Montana Water Quality Act (75-5-102, MCA) goals and protections for Montana's water resources.

Montana's pH standards vary between beneficial use classes but are mostly based on limiting variance within a predetermined range of acceptable pH values. Montana WQS are exceeded when an induced variation is ≥0.5 units within an indicated pH range, or if pH is induced to change by any amount when the natural pH is outside an indicated range. The exceptions are Class A-Closed waters that do not allow for any change from the natural conditions and Class I waters that must maintain pH within a specified range.

Montana's pH WQS are contained in the Administrative Rules of Montana (ARM) 17.30.621 through 17.30.629. **Table 1** displays the different standards for each of Montana's primary beneficial use classes.

Table 1. Montana's pH Standards

Use Classes	Applicable Standard
A-Closed	No change from natural pH is allowed.
A-1, B-1, C-1	Induced variation of pH within the range of 6.5 to 8.5 must be less than 0.5 pH unit. Natural pH outside this range must be maintained without change. Natural pH above 7.0 must be maintained above 7.0.
B-2, B-3, C-2, C-3	Induced variation of pH within the range of 6.5 to 9.0 must be less than 0.5 pH unit. Natural pH outside this range must be maintained without change. Natural pH above 7.0 must be maintained above 7.0.
I (Impaired)	Hydrogen ion concentration must be maintained within the range of 6.5 to 9.5.

3.0 MONITORING DESIGN AND ASSESSING DATA QUALITY

Montana's numeric WQS are written as hydrogen ion concentrations (pH 0 to 14). pH is the only data type that is to be applied directly to the Montana pH WQS. Waterbody condition must be evaluated based on all existing and readily available water quality-related data and information (§75-5-702, MCA; 40 CFR 130.7[b][5]).

This section describes considerations for developing monitoring designs and assessing data quality when performing pH assessments. This section is not intended to limit data collection and is only provided as guidance. Additional monitoring guidance is provided in the following Standard Operating Procedure (SOP) documents for use of continuous dataloggers and/or handheld meters while collecting data:

- Multiparameter Water Quality Sondes SOP (Milke 2025)
- Small Water Quality Dataloggers SOP (McWilliams and Nixon 2020)
- Instantaneous Field Meter SOP (McWilliams and Bushnell 2025)

3.1 Minimum Data Requirements

Assessment methods provide minimum data requirements to initiate an assessment. Since DEQ must use all readily available and credible data, these minimum requirements are provided for initiating an assessment of how pH may affect aquatic life.

To provide the ability to screen more data across the state, DEQ uses a minimal dataset necessary for screening if there are pH problems, and generally requires more data to prove a use is supported. The highest data requirement is used for removing an existing pH listing. This approach provides a system that can screen smaller datasets and still provides protection of aquatic life. This section should not be interpreted to limit data collection but is provided to set minimum expectations for proceeding with a pH assessment under the Clean Water Act beneficial use assessment program in Montana.

Due to the type of data evaluated by DEQ, multiple approaches exist for determining the minimum data needed to proceed with a pH assessment. Each approach has specific constraints regarding the minimum data quantity, temporal requirements, and associated decision-making limitations. Given that pH levels in a waterbody often fluctuate diurnally and seasonally, it is essential that datasets adequately capture this variability to support an accurate assessment of use attainment. **Table 2** outlines the different scenarios available to assessors for conducting use attainment evaluations, including the criteria and limitations applicable to each.

Table 2. Minimum data requirements for use attainment scenarios

Data Type	Number of Samples	Temporal Requirements	Decision Making Limitations
Continuous Data	5 complete days	Outside of the growing season	Can determine impairment **but not** use support
	5 complete days	Within the growing season	Can determine either impairment or use support
Discrete Data	5 grab samples	From 5 separate days outside of the growing season	Can determine impairment **but not** use support
	10 grab samples	Representing daily minimums and maximums from 5 days within the growing season	Can determine either impairment or use support
	Large dataset *	Any time of day, any days of the year; but adequately represents the growing season	Can determine either impairment or use support

* Large discrete datasets, as well as all other data types, are addressed in more detail in **Section 3.1.1**.

For pH assessments, all available data, including each discrete measurement, will be evaluated to determine if pH stayed within the appropriate pH standard range applicable to the waterbody's use class. If quality continuous data are available for the same site and timeframe as discrete data, continuous data supersede discrete. This is because continuous monitoring allows for assessment of changes in pH throughout the day that cannot be captured with a single sample (EPA 2021).

3.1.1 Use Support Data Types

Continuous Data

Continuous data used for assessments should be collected at equal intervals of 1-hour or less (i.e., 15- or 30-minute intervals). Collecting continuous data is the preferred approach for pH assessments.

5 Complete Days (outside of the growing season): When continuous pH data are available for at least five complete days outside of the growing season the dataset can be used to determine if the waterbody does not support the aquatic life beneficial use. However, this is not sufficient data to conclude that the waterbody is fully meeting WQS due to the lack of data from sensitive timeframes.

5 Complete Days (within growing season): If continuous data include five complete days within the growing season, it provides stronger evidence of the waterbody conditions during sensitive timeframes. This allows for both determinations: if the waterbody is impaired or if it is meeting the beneficial use.

Discrete Data

A minimum of five discrete (grab) samples are required to determine if the use is not supported. Discrete data are not preferred for assessment because it is difficult to determine if adequate daily minimum and maximum data have been collected to represent conditions that fully support aquatic life.

5 Grab Samples (from 5 separate days outside of the growing season): With only five discrete grab samples (taken at any time during the year **but** from five separate days), the dataset is limited. The data can indicate impairment when obvious sources are present but are not sufficient to conclude if the waterbody is meeting WQS. This is not the preferred monitoring design but can be used on any readily available data.

10 Grab Samples (daily min/max, within growing season): Ten grab samples collected to represent five days of daily minimums and maximums during the growing season offer more comprehensive temporal coverage. This scenario allows for determinations of both impairment and beneficial use attainment. See **Section 3.4** for daily monitoring timeframes to achieve requirements for daily minimum and maximum monitoring. This method is only recommended if continuous dataloggers are not available for use.

Large Dataset: A large discrete dataset that adequately covers both seasonal and diurnal variability provides robust information. It supports making both types of decisions: identifying impairments and confirming if WQS are being met. An assessor should consider secondary indicators to determine whether pH is fully supporting the use when a large, discrete dataset passes exceedance testing but lacks five days of daily minimum and maximum samples, as long as the data represent growing season conditions. Secondary indicators to consider may include response variables or influencing factors, such as algae or macrophyte growth, macroinvertebrate or other biological data, and watershed geology.

Before using this approach to make a “fully supporting” determination for pH, sources of pollution (e.g., eutrophication, industrial or urban runoff, abandoned or active mines) should be confirmed as absent or minimally present in the watershed. This approach cannot be used if municipal or industrial permitted point sources are present and discharge directly to an assessment unit (AU).

3.1.2 Assessing Shifts In pH

If paired data are available both above and below any discrete sources on an AU and collected at the same times, it must be evaluated for a shift in pH. If paired data is available from the discrete source and directly upstream of the source, a mixing calculation should be used to determine the source's effect on the receiving water. A calibrated model based on data collection may also be used to assess shifts in pH. See **Section 4.2** for possible data interpretation and assessment outcomes.

3.1.3 Removal from the Impaired List

For a waterbody to be delisted, at least 15 complete days of data are required to be collected during the growing season (See Suplee and Sada 2016 and Clift *et al.* 2024 for growing season dates). A more extensive dataset will demonstrate the waterbody is meeting pH standards diurnally and seasonally. Data for delisting must include multiple sites that represent all conditions and sources within the AU. This includes a site or sites that best represent the largest diversion from natural conditions, in an area where sources affecting pH are located. **Table 3** shows the minimum data requirements required for delisting an AU.

Table 3. Minimum data requirements for delisting

Data Type	Number of Samples	Temporal Requirements	Decision Making Limitations
Continuous	15 complete days	Within the growing season	Can determine either impairment or use support
Discrete	30 grab samples	Representing daily minimums and maximums from 15 days within the growing season	Can determine either impairment or use support

For delistings, a reference site should be monitored within or near the AU that can reasonably be shown to represent natural pH conditions. A site representing natural pH may be established in another AU so long as the secondary AU is continuous or in the general region and comparable with the AU being assessed and the site can reasonably be shown to:

a) represent natural pH, and
b) have similar hydrologic and geomorphic characteristics compared to the AU being evaluated.

Appropriately matched reference waterbodies should be used to characterize any shift in pH. Data, mixing calculations, and potentially modeling if sources are complex, must be able to evaluate if sources cause a shift in pH, and if so, the extent of the shift. If there are major point sources directly discharging to the AU, this approach must be used to adequately assess the induced variation.

3.2 Monitoring Timeframes and Data Independence

This section provides guidance on selecting appropriate times to sample for pH, with the goal of ensuring temporal independence between sampling events. Because pH conditions can fluctuate hourly, pH samples are typically more temporally independent than many other water chemistry parameters. This guidance is not intended to restrict data collection efforts.

3.2.1 Time of year

Measurement of pH data can be undertaken at any time of the year, as pH standards are applied year-round. pH conditions in Montana's waters are influenced by increased or decreased amounts of CO_2 when plant, algae, or bacterial respiration occurs through photosynthesis. This typically occurs during the warmest times of the year, when respiration rates are highest in a given waterbody.

Other anthropogenic activities, such as eutrophication (**Section 1.3.1**), acid mine drainage (**Section 1.3.2**), and those outlined in **Section 1.4** may affect pH at any time of the year. Therefore, when designing a study, data collection should target a portion of the growing season. However, peak senescence and non-growing season timeframes may also be targeted if decomposition, biochemical oxygen demand, acid mine drainage, or dam operation is suspected as a driver of pH departures from WQS.

3.2.2 Time of Day and Frequency

pH data can be collected during any time of the day for assessment use. However, the daily cycle of pH that may be influenced by photosynthesis and respiration should be represented in the data (minimum and maximum values) in order to perform analysis for assessment efforts.

Rivers and streams normally display a sinusoidal pH pattern during the growing season in Montana. pH typically drops throughout the night and is at its lowest in the pre-dawn hours. The highest pH values will generally occur in the afternoon/evening hours. It is recommended to use a continuous datalogger to capture these timeframes for assessment purposes. However due to sampling constraints, one discrete sample collected from each of these timeframes (see **Section 3.4** for specific times) is considered to be representative for general evaluation purposes. This guidance may not fully apply if acid mine drainage is affecting an AU with low eutrophication, and best professional judgement should be used to determine the best times to monitor the AU.

3.3 Monitoring Locations and Spatial Independence

This section contains guidance for selecting sampling locations and is intended to help gain spatial independence between sites during data collection.

3.3.1 Assessment Unit Selection

pH assessment decisions are made on the individual AU scale. Guidance for determining AU delineations can be found in DEQ's Beneficial Use Assessment Method (Makarowski 2020). An AU may be an entire waterbody or segment of a waterbody (e.g., headwaters to a tributary). DEQ or other entities may prioritize monitoring of waters that have been previously identified as impaired or waters at higher risk of pH impairment due to human activities, point sources, agricultural use, or other factors. All readily available data must be included for assessment of any AU that is part of a 303(d)-assessment project.

pH assessment determinations will be made by looking at data available throughout the entirety of an AU. Although more sites are generally desired, only one site per AU is needed if that site is located in the most at-risk area (that is, downstream of the most intensive source area). However, additional sites are necessary for determining if pH is supporting the use and best professional judgement should be used to determine how many sites are needed to represent the range of potential human and natural sources influencing the AU. To delist an AU, sites need to represent the conditions of the entire AU along with the most at-risk area.

3.3.2 Spatial Independence

Sites should be spatially independent of one another in order to capture as much variance throughout an AU as possible. Spatial independence relies on best professional judgement, particularly when combining data from multiple sources and projects. Considerations will be made for available data types and what scale to complete each AU's assessment (See **Section 4.3**). The following guidance for achieving spatial independence for pH monitoring aligns with similar guidance in DEQ's other assessment methods (Suplee and Sada 2016; Drygas 2012):

- Select sites that are at least one mile apart; unless there are abrupt natural or manmade changes in physical or chemical conditions created by tributaries, geology, landforms, land use, or point source and nonpoint source discharges.
- Monitor outside of Montana Pollutant Discharge Elimination System mixing zones.
- Monitor below areas where tributaries or ditches mix with the AU.
- Consider land use and geology to help identify potential sources of altered pH.

3.3.3 Assessment Reaches

If a relatively unimpacted upstream reach can be isolated, and its condition is presumed substantially different from other downstream parts of the AU, the AU may be split into sub-units or "reaches" for assessment purposes. The following rules will apply to reaches:

- If any reach indicates impairment, the entire AU receives the impairment determination.
- Each reach has the same data requirements as the parent AU would have had if it had not been divided.
- It is more beneficial to retain larger reaches to avoid excessive segmentation and the consequential addition of administrative and sampling requirements that result.

3.4 Monitoring Design Recommendations

Continuous vs. Discrete

To ensure that the daily minimum and maximum values are captured, DEQ highly recommends using continuous pH measurements over discrete. If using discrete data only, measurements should be collected both between 4:00 am and 8:00 am to capture the daily minimum, and between 2:30 pm to 5:00 pm to capture the daily maximum. Depending on known existing factors influencing an individual AU or reach (e.g., eutrophication or acid mine drainage), it may not be necessary to collect both a morning and evening sample. The monitoring design should consider what pH conditions are likely to be encountered, and efforts should focus on the times of day that will most likely capture excursions from the applicable WQS.

Source Assessment

Sites that represent the areas that have both high and low anthropogenic sources should be included when designing a project for pH assessment. Sites should also bracket sources including agricultural runoff, wastewater treatment outfalls, and historic and current mining operations (EPA 2023).

Spatial

It is preferable to collect data at multiple sites to represent the entire AU and better capture variability in pH, and this approach is necessary for delisting. The recommended number of sites is two or more within an AU with at least one necessary to represent the most at-risk area for initiating listings.

Temporal

If monitoring resources are limited, monitoring should occur during months where aquatic plant and algae growth is most prevalent and when streamflow is relatively low. This will enable the data to encompass the most critically sensitive time of year when seasonal maximums or minimums are likely to occur (i.e., the growing season).

3.5 Data Quality

Established policies and procedures of DEQ's Water Quality Division for Quality Assurance and Quality Control (QA/QC), beneficial use assessment, and data management apply to this assessment method. Data quality requirements apply to all data included while making use attainability decisions, whether collected internally (by DEQ) or externally.

3.5.1 Data Quality Assessment Overview

Data quality assessment (DQA) is the scientific and statistical evaluation used to determine whether data obtained from monitoring operations are of the right type, quality, and quantity to support water quality assessments (EPA 2002). Assessors use DEQ's Water Quality Assessment and Reporting Documentation (WARD) system to document the DQA outcomes (e.g., pass or fail) for each parameter group being assessed per beneficial use. All data quality indicators must be met to pass the DQA; if a single indicator is not met, the DQA fails for that parameter group. An assessor may override pass or override fail a DQA determination, but they must accompany this override with adequate justification. Additional data quality screening may be necessary before the dataset is ready to support attainment decisions (EPA 2002), for example:

- Reviewing and rectifying changes in measurement values after a sensor cleaning event
- Evaluating database flags
- Evaluating QC samples (i.e., field checks)
- Reviewing QA/QC reports
- Investigating errors in collection or analysis
- Addressing missing data
- Reviewing deviations from SOPs and sampling and analysis plans
- Reviewing percent change from previous and subsequent measures from dataloggers
- Documenting when calibration occurred and reviewing instrument calibration logs

Once DEQ determines the data meet basic documentation requirements, the data are ready to be analyzed to support WQS attainment decisions (EPA 2002).

3.5.2 Quality Control

Measurements of pH in the field are commonly collected using potentiometric pH meters, which determine pH by using the electrical potential of pH-sensitive electrodes as a measurement signal (Cushman 2019). These devices are typically available as handheld instantaneous field meters or submersible continuous dataloggers.

Proper calibration in accordance with **each manufacturer's guidance manual is essential**, and calibration logs **must** accompany any data submitted to DEQ to be used for pH beneficial use assessments. Additionally, any sensor replacement or maintenance activities should be included in the log. If sensors are not replaced according to the manufacturer schedules, data will usually drift upward. All instruments used for assessment must adhere to the manufacturer's calibration and maintenance schedules, with calibrations documented and summarized in a post-collection QA/QC analysis. For guidance on operation, applicability, and data collection procedures, refer to the to the Standard Operating Procedures mentioned in **Section 3.0**.

All data are subject to QA/QC checks by the assessor before use in assessments. A QA/QC review of field meter calibration, post-deployment data review, and a post-deployment audit is mandatory for DEQ to consider pH data.

3.5.3 Data Currency

Data collected within the past ten years is considered current and may be used in making assessment decisions (Makarowski 2020). If during this period significant changes in pollutant sources have been documented, the assessor may use best professional judgement to determine which data are appropriate to include in the assessment. The assessor should document the specific changes, identify data currency alternatives, and determine which years of data are appropriate to include in the assessment process.

4.0 Data Analysis to Support Attainment Decisions

This section describes how pH data will be prepared and analyzed for assessment. pH is the only data type that is to be applied directly to the Montana pH WQS.

4.1 Overview of the Assessment Approach

For each AU, data will be compiled, evaluated for quality, and prepared for assessment as outlined in **Section 4.3**. The data will be analyzed, and the results will be compared to the pH WQS in **Section 2.0**. Based on the data analysis, the assessor will determine if sites are meeting or exceeding the WQS or if they have insufficient information for assessment.

The core of DEQ's screening approach will follow EPA guidance outlined in the Blue Book (EPA 1972) to ensure Montana waterbodies remain within the WQS ranges in **Section 2.0.** These ranges were developed to ensure that no harm would occur to the most sensitive beneficial use and provide an easy-to-use framework for initiating assessment.

Additionally, Montana's WQS include the term "induced variation". Induced variation refers to changes in the pH level of a waterbody that are caused by human activities or external influences as opposed to natural fluctuations. However, determining induced variation may only be possible through detailed source monitoring (targeted and paired monitoring up-and-downstream) or if a calibrated model of the waterbody exists. If either of these resources are available, the assessor must rely on the additional data or the model to assist them in making their attainment decision to assess the induced variability of pH. Many times, this information will not be available.

The prevention of induced variation ensures that even when staying within the broader acceptable ranges associated with each use class, anthropogenic changes do not disrupt aquatic ecosystems that may be sensitive to small shifts in pH.

4.2 Assessment Decision Framework

Because federal pH WQS guidance provides a range of pH to stay within, and the beneficial use assessment program is a screening program designed to protect beneficial uses, the first step in analysis will be to determine if conditions generally fall within Montana's pH ranges. The range applied for the analysis depends on the use classification of the AU (**Table 1, Section 2.0**). This step is applicable to all waters except those under the A-closed use class, which allows for no change from natural pH.

All collected data will first be evaluated using daily statistics, followed by an analysis of the full dataset. A day is considered in exceedance of the WQS when >10% of the samples (discrete and/or continuous) fall outside the ranges provided in **Section 2.0**. Once individual days are identified as exceeding (>10% of samples outside the applicable range), the total number of such days will be compared to the critical values in **Appendix B**, which are derived from an exact binomial statistical analysis. An AU will be considered impaired when the number of daily values that exceed WQS surpass the applicable critical value based on the number of total daily values in the dataset.

4.2.1 Impairment to Beneficial Use (Listing)

DEQ will use the applicable range to complete initial exceedance screenings. If pH falls outside the range of pH in Montana's standard for the AU and there are probable sources affecting the pH, the assessor will indicate a pH impairment and listing. If sources can be discerned from monitoring results that contribute a 0.5 induced variation in pH, even when the pH falls within the range, then source information based on pH monitoring should be used in assessment determinations. If >10% of paired source assessment samples, or >10% of the modeled timeframe indicates an induced variation of greater than 0.5 units, the assessor will indicate a pH impairment and listing.

A-Closed

Targeted monitoring up-and-downstream of potential sources and a calibrated model should be used to determine natural conditions. Sources should be evaluated to determine if any shift in pH occurs.

A-1, B-1, C-1

If anthropogenic or other potential sources of pH variations are present in the watershed, the AU should be listed as impaired if sample data are outside the range of 6.5-8.5 in greater than or equal to the critical value of the corresponding daily values. If detailed source monitoring data and/or a model of the watershed is available, evaluate the induced variation within the range.

B-2, B-3, C-2, C-3

If anthropogenic or other potential sources of pH variations are present in the watershed, the AU should be listed as impaired if sample data are outside the range of 6.5-9.0 in greater than or equal to the critical value of the corresponding daily values. If detailed source monitoring data and/or a model of the watershed is available, evaluate the induced variation within the range.

I (Impaired)

If anthropogenic or other potential sources of pH variations are present in the watershed, the AU should be listed as impaired if sample data are outside the range of 6.5-9.5 in greater than or equal to the critical value of the corresponding daily values. No shift in pH is included in this standard.

4.2.2 Use Support and Removal from the Impaired List (Delisting)

Delisting an impaired AU involves a higher level of confidence and statistical significance when compared to initially listing. The data collected during the monitoring process need to show sustained improvements to ensure they are not just a temporary fluctuation or random variation. Because of this, DEQ requires ample data to be collected during the growing season for delisting an individual AU. A longer monitoring period allows for a more accurate assessment of the overall water quality trends and ensures that the improvements are consistent and sustained both diurnally and seasonally.

A-Closed

Targeted monitoring up-and-downstream of potential sources and a calibrated model should be used to determine natural conditions. Sources should be evaluated to determine if any shift in pH occurs.

A-1, B-1, C-1

If anthropogenic or other potential sources of pH variations are present in the watershed, the AU should be delisted as impaired if sample data are within the range of 6.5-8.5 while using the critical value of the corresponding daily values. Additionally, a detailed source assessment must indicate a cumulative shift of less than 0.5 units. If detailed source monitoring data and/or a model of the watershed indicates natural conditions are outside the range and there is no induced variation, the assessor may also pursue a delisting.

B-2, B-3, C-2, C-3

If anthropogenic or other potential sources of pH variations are present in the watershed, the AU should be delisted as impaired if sample data are within the range of 6.5-9.0 while using the critical value of the corresponding daily values. Additionally, a detailed source assessment must indicate a cumulative shift of less than 0.5 units. If detailed source monitoring data and/or a model of the watershed indicates natural conditions are outside the range and there is no induced variation, the assessor may also pursue a delisting.

I (Impaired)

If anthropogenic or other potential sources of pH variations are present in the watershed, the AU should be delisted as impaired if sample data are within the range of 6.5-9.5 while using the critical value of the corresponding daily values.

4.3 Data Analysis Procedure

DEQ will compare both continuous and discrete data against a given AU's respective WQS. This process will include using an exact binomial test (previously indicated as critical value term above), which will enable assessors to determine impairment status based on the number of exceedances present in the dataset. The process is outlined in the steps below:

1. Determine the waterbody use class to determine the applicable WQS pH range (**Section 2.0**).
2. Perform DQA to identify the usable dataset (**Section 3.5**).
3. Compile all pH data for an AU.
    a) If there are continuous data, or discrete data that meet the 5-day min/max requirements for an AU, pH data will be analyzed on a site-by-site scale.
    b) If there are only discrete data for an AU that do not meet the 5-day min/max requirement, pH data will be analyzed on the AU scale.
    c) Organize samples by date and time.

    a) If there are continuous and discrete data for the same day and time, the continuous data supersedes the discrete.
  d) Data from sites that meet the 5-day min/max requirement supersede sites that do not, unless discrete data is demonstrated to be collected at more high-risk location(s) and shows impairment.
4. Assess exceedances of the applicable WQS pH range with the exact binomial test.
    a) Additional guidance for this step is provided to DEQ staff in **Appendices A and B**.
    b) Document the outcome of the test and review potential sources if the test fails.
5. If detailed source monitoring data and/or a model of the watershed exists, use it to evaluate potential induced variation in pH.
    a) Identify potential sources of influence.
        a) Use available source monitoring data to determine whether localized discharges, irrigation returns, or impaired tributaries correspond spatially or temporally with observed pH shifts in the assessment dataset.
    b) Evaluate spatial patterns.
        a) Review the longitudinal profile of pH along the waterbody (upstream to downstream) and compare with modeled or observed source inputs to determine whether variations in pH align with known or predicted zones of influence.
    c) Document relationships.
        a) Summarize any statistically or visually apparent associations between pH variation and specific sources or watershed processes (e.g., eutrophication, acid mine drainage, algal productivity).
    d) Quantify induced variation.
        a) If a watershed or water quality model is available, use it to simulate background (unaffected) conditions and compare those to the observed data to estimate the magnitude of anthropogenic pH change. Use the available calibrated model to assess cumulative sources including non-discrete source effects.
    e) Integrate findings into assessment.
        a) If induced variation is demonstrated, determine whether it indicates impairment, natural variability, or a condition driven by identifiable sources that may warrant follow-up monitoring or management action.
6. Use the assessment guidance to determine if pH:
    a) Has insufficient information
    b) Is fully supporting uses (Use determination outcomes “Do Not List” or “Delist”)
    c) Is impairing aquatic life use (Use determination outcomes “List” or “Keep Listed”)

4.4 Assessment Documentation

The assessor must document all data and decisions made pertaining to pH impairment and beneficial use support determinations for each AU. Assessment outcomes for individual AUs, including data summaries, impairment decisions, and beneficial use support determinations are documented via DEQ’s WARD database. Assessment decisions are also reviewed by the Monitoring and Assessment Section Supervisor and may be reviewed by the QA Officer and managers or staff from other DEQ programs.

Waterbodies identified as impaired due to pH are included in Montana’s Water Quality Integrated Report and list of impaired waters; pH impairments are then addressed in TMDL documents through identification of causal pollutants, often (but not always) metals or nutrients. pH data collected by DEQ is stored in the Montana EQuIS Water Quality Exchange database and is uploaded regularly to the National Water Quality Portal. DEQ's Clean Water Act Information Center reports all decisions and results to the public.

4.4.1 Integrated Reporting Categories

Montana uses a system of reporting categories to summarize the impairment status for each AU. Categories range from Category 1 (fully supporting all uses) to Category 5 (one or more uses is impaired by a pollutant and requires a TMDL). Categories describe impairment status for AUs but are also used to describe individual AU-cause combinations. More information on reporting categories is described in the Beneficial Use Assessment Method for Montana's Surface Waters (Makarowski 2020).

5.0 References

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APPENDIX A – STATISTICAL ANALYSIS STEPS

This stepwise procedure provides guidance for DEQ staff conducting pH beneficial use assessments using both continuous and discrete water quality data. It outlines how to process, analyze, and interpret pH data in accordance with state WQS to determine whether a waterbody should be listed or delisted for pH impairment. The instructions describe how to format and analyze continuous pH data using the statistical computing tool "R", evaluate discrete sample results, and compare exceedances against the statistical critical values provided in **Appendix B**. The process concludes with combining continuous and discrete datasets for final listing determinations. All corresponding files referenced in this section are stored on the WQ drive at the following location: G:\WQP\7_QAProgram\5_Assessment_Methods\pH\Assessment_Tools.

Continuous Data

1. Open the "pH_Assessment_Template" file. Save the file under a new name for each assessment.
2. Paste data from the continuous datalogger Blob file into the "C_RAW DATA Station #" tab.
3. Copy and paste the appropriate columns from the "C_RAW DATA Station #" tab into the "Template_ContinuouspH_R.xlsx" file, following the instructions in the spreadsheet.
    a) Ensure the date column is formatted as "YYYY- MM-DD" so the R code runs correctly.
4. Open the "ContinuouspH_AM.R" file in RStudio to run the statistical analysis code.
    a) Before running the code:
        i. Update line 18 to reflect the input file name you created in **Step 1**.
        ii. Update line 30 to reflect the correct WQS pH range values.
        iii. Update line 32 to specify the number of samples per day (ex., 96 samples for 15-minute time intervals).
5. Run the R code. The program will generate an output file summarizing the number of exceedances of the WQS pH range per day. Copy and paste these results into the "C_ASSESSMENT_Station #" tab of the assessment file created in **Step 1.**
6. Calculate 10% of the total number of samples per day (e.g., 10% of 96 samples = 9.6). For each day, compare the number of exceedances to this 10% value, and record how many days exceed the 10% threshold.
7. Refer to **Appendix B** to find the critical value that corresponds to the total number of daily values in your dataset (e.g., for 96 daily values, the critical listing value is 14).
    a) Compare the total number of days that exceed the 10% threshold to the critical value to determine if the site meets or exceeds the listing criteria.
8. If there are incomplete days of continuous data (i.e., days where equipment was deployed or retrieved) paste that data into the "D_ASSESSMENT_Station #" tab for the corresponding station.
    a) Find the minimum and maximum values of pH for those incomplete days.
    b) These values will be combined with any discrete data from the same site and assessed as described in the **Discrete Data** section below.
9. Combine all continuous and discrete data for the same site to determine the total number of observations and exceedances.
    a) **If the total number of daily values with exceedances is greater than or equal to the critical value and anthropogenic sources are present, the listing decision is "List" or "Keep Listed."**

b) **If the total number of daily values with exceedances is less than the critical value, the listing decision is "Do Not List" or "Delist." Review delisting data requirements before finalizing a delisting determination.**

Discrete Data

1. Calculate how many discrete samples fall outside the corresponding WQS pH range.
    a) Document the number of days with exceedances. If there are multiple discrete samples from the same day: Calculate 10% of the total number of samples per day. For each day, compare the number of exceedances to this 10% value, and record how many days exceed the 10% threshold.
2. Refer to **Appendix B** to find the critical value that corresponds to the total number of daily values in your dataset.
3. Compare the total number of days that exceed the 10% threshold to the critical value to determine if the site meets or exceeds the listing criteria.
    a) **If the total number of daily values with exceedances is greater than or equal to the critical value and anthropogenic sources are present, the listing decision is "List" or "Keep Listed."**
    b) **If the total number of daily values with exceedances is less than the critical value, the listing decision is "Do Not List" or "Delist." Review delisting data requirements before finalizing a delisting determination.**

APPENDIX B – BINOMIAL TABLES

These tables were created using DEQ's Noncompliance Tool, which utilizes statistical analysis to compare observed data against a null hypothesis (no exceedance of WQS). The tool calculates the proportion of samples that exceed the WQS and evaluates this against confidence interval thresholds to determine whether exceedances are statistically significant. These tables show the total number of daily values in the dataset and the corresponding number of exceedances (critical value) required to list or delist an assessment unit.

Impairment to Beneficial Use (Listing or Do not list)	
Daily Values	**Critical Value**
5-11	3
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
139-147	20
148-156	21
157-164	22
165-173	23
174-182	24
183-191	25
192-199	26

<u>Null hypothesis:</u> Actual exceedance proportion is ≤10%
<u>Alternate hypothesis:</u> Actual exceedance proportion is >10%
Minimum confidence level is 90%
A minimum of five daily values is required

Use Support and Removal from the Impaired List (Delisting)	
Daily Values	**Critical Value**
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
148-156	19
157-164	20
165-173	21
174-182	22
183-191	23
192-199	24

<u>Null hypothesis:</u> Actual exceedance proportion is >10%
<u>Alternate hypothesis:</u> Actual exceedance proportion is ≤10%
Minimum confidence level is 90%
A minimum of fifteen daily values is required

<u>Note:</u> If a dataset has sample sizes greater than 199, the assessor will calculate the critical value using the Montana DEQ Noncompliance Tool. In the NonCompliance Tool, assessors will set the values for alpha, p1, and p2. In cell L16 (Specify N*), the assessor will input the sample size and the tool will calculate the critical value (e).