APPENDIX F

pH LISTING METHODOLOGY

NEW MEXICO ENVIRONMENT DEPARTMENT
SURFACE WATER QUALITY BUREAU

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Purpose and Applicability

This document establishes a listing methodology for determining impairment due to pH excursions in streams, rivers, lakes, and reservoirs. This protocol is not applicable to streams with limited aquatic life use and wetlands because the research and implementation procedures necessary have not been investigated or developed by the Surface Water Quality Bureau (SWQB) or adopted in 20.6.4 NMAC.

1.0 Introduction/Background

The pH of a solution is a measure of its acidity or basicity and is calculated as the inverse log of the hydronium ion concentration ($pH = -\log_{10} [H_3O^+]$). In water, pH is a measure of the acid-base equilibrium resulting from various dissolved compounds and gases. A pH value of 7.0 is considered neutral. That is, at pH 7, the concentration of hydrogen ions ($[H^+]$) is equal to that of hydroxide ions ($[OH^-]$). The principal buffering system regulating pH in natural waters is the carbonate-bicarbonate system, composed of carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate ion (HCO_3), and carbonate ion (CO_3). Gradual, non-linear deterioration of a waters ability to support aquatic life occurs as pH values depart from neutral. A range of pH values from 5.0 to 9.0 is not directly lethal to fish; however, the toxicity of some pollutants (e.g., ammonia) can be substantially affected by pH changes within this range (EPA 1986). At pH values above 9.0, fish have difficulty excreting ammonia across the gill epithelium.

In New Mexico, typical pH values in surface waters that are largely unaffected by anthropogenic disturbance vary approximately from 7.5 to 8.7. An exception, Sulphur Creek in the Jemez River watershed, has documented natural background pH values as low as 2.4 as a result of parent lithology and geothermal influences. Accordingly, segment-specific criteria have been established for this stream.

2.0 Data Collection Procedures and Considerations

An increase in pH values can result from the decrease of carbonic acid when carbon dioxide, carbonate, and bicarbonate are used by plants during photosynthesis. Thus, when high levels of nutrients lead to excessive plant productivity, pH values above 9.0 may occur during the daylight hours. During the night, when photosynthesis does not occur, the pH value drops. The result is a daily or "diel" fluctuation of pH values that lags behind the diel fluctuation observed in dissolved oxygen concentrations. Dissolved oxygen (DO) concentration is at its lowest in the early morning in areas of excessive aquatic plant growth. This is in contrast to the diel pattern of pH values, which are most likely to have an excursion of the criteria late in the day. For these reasons, it is best to use continuous recording devices (sondes) to record pH values, especially where excessive aquatic plant growth is evident.

The SWQB typically deploys sondes to record DO, pH, specific conductance, temperature, and turbidity values over a specific period of time. Sondes are deployed and the data reviewed following the guidelines specified in the SWQB Standard Operating Procedures (SOPs, available at: https://www.env.nm.gov/swqb/SOP/). Sondes should be used to collect pH data in order to

observe a more complete picture of any diel fluctuations, as opposed to the "snapshot" that grab data provide; however, in some cases only grab data are available. For rivers and streams, sonde data sets deployed for ≥72 hours with a maximum one-hour frequency interval are preferred for assessment purposes and required to determine Full Support of the applicable criteria. For SWQB collected data, additional information regarding the preferred timing of sonde deployment is typically provided in applicable Field Sampling Plans or Water Quality Survey Reports (available at: https://www.env.nm.gov/surface-water-quality/water-quality-monitoring/). The likelihood of capturing adequate data to determine natural vs. anthropogenic influences to pH concentrations increases with increased sonde data, so longer sonde deployments with interim equipment checks and data downloads are encouraged. pH listings based on grab data from streams or rivers will be noted as Category 5C (i.e., needing sonde data to confirm).

The SWQB is exploring the feasibility of sonde deployment in lakes and reservoirs. If it is determined that sondes can be safely deployed in this waterbody type and generate valuable data that can meet 20.6.4.14.C(3) NMAC, the SWQB will develop a standard operating procedure and listing methodologies for lake sonde data.

3.0 Assessment Procedure

New Mexico pH criteria found in 20.6.4.900.H NMAC (available at: http://www.nmenv.state.nm.us/swqb/Standards/) are based on the aquatic life use designation (Table 1). There are two segment-specific pH criteria (2.0 - 8.8) for Sulphur Creek (20.6.4.108 and 20.6.4.124 NMAC).

Table 1. New Mexico's pH criteria

Aquatic Life Use	pH Range
High Quality Coldwater Coldwater	6.6 to 8.8
Marginal Coldwater Coolwater Warmwater Marginal Warmwater	6.6. to 9.0
Limited	No default established

Sonde data sets greater than 72 hours with a maximum one hour frequency interval are required to assess with the continuously recorded data set assessment method in Table 2. If this resolution of sonde pH data is not available, the instantaneous grab method is used to determine attainment. pH impairment listings determined from grab data for streams and rivers will be noted as Category 5C and prioritized for sonde deployment to confirm the assessment.

Table 2. Determination of aquatic life use support using pH data

TYPE OF DATA	FULLY SUPPORTING	NOT SUPPORTING	NOTES
•Instantaneous (grab) pH data			
A) Rivers or streams	**A)** Not assessable (cannot determine Fully Supporting with grab data only)	**A)** pH is outside the criteria range in >10% of measurements, or more than one measurement if 4* to 10 data points are available.	**A)** pH listings based on grab data will be noted as Category 5C (need sonde data to confirm).
B) Lakes or reservoirs	**B)** No pH criteria excursions^	**B)** 1 or more pH criteria excursions^	**B)** See 20.6.4.14.C(3) NMAC for additional information regarding lake sampling.
•Continuously recorded pH data (≥72 hours, ≤ one hour frequency interval)	pH criteria excursion(s) for <u>less than four</u> consecutive hours.	pH criteria excursions for <u>four or more</u> consecutive hours.	

NOTES: * Less than 4 samples = not assessed. See Section 2.1.4 Main Listing Methodology (CALM) for details.
^ Lakes are typically sampled once in the spring and fall, and twice in the summer. pH measurements taken at intervals are averaged for the epilimnion, or in the absence of an epilimnion, for the upper one-third of the water column of the lake to determine attainment of pH criteria.

<u>REVISION HISTORY:</u>

2014 listing cycle – Minor clarifications.

2016 listing cycle – Removed pH 9.5 upper threshold because not supported in EPA's pH criteria guidance (EPA 1986). Reduced grab data Non Support for lakes and reservoirs to 1 or more excursions because lakes and reservoirs are typically sampled once in the spring and fall, and twice in the summer; each seasonal sampling event is intended to be representative of the entire season. Changed 24-hour floating average approach to more conservative 4 consecutive hour approach to better align with existing pH water quality standards and DO assessment protocol.

2018 listing cycle – "Assessment Protocol" changed to "Listing Methodology." Removed Table 2 note regarding pH as a nutrient response variable because pH is no longer a response variable in the nutrient listing methodology. Changed Table 2 from "10 or fewer" to "2 to 10" because n=2 is a minimum data requirement for assessment (added related footnote).

2020 listing cycle – Added reference to SWQB Field Sampling Plans for additional sonde deployment information.

REFERENCES:

U.S. Environmental Protection Agency (EPA). 1986. Quality criteria for water 1986. Washington, D.C. Available at: http://water.epa.gov/scitech/swguidance/standards/criteria/current/upload/2009_01_13_criteria_redbook.pdf.