

TCEQ Implementation of Texas Surface Water Quality Standards (30 TAC §307) pH Criteria

Background - pH Criteria

EPA's national guidance criterion for pH in fresh water is a range of 6.5-9.0 Standard Units (s.u.) based upon the 1986 EPA "Gold Book" compilation of criteria. As with other long-standing national criteria, TCEQ has adjusted the pH range where appropriate using local monitoring data. Many of these adjustments were made during previous revisions to the Texas Surface Water Quality Standards (TSWQS), but this process still continues. In the 2010 TSWQS revisions, the criterion for Caddo Lake (Segment No. 0401) was "re-adjusted" from 6.0 - 8.5 s.u. to 5.5 - 9.0 s.u., for example. This practice is consistent with §131.11(b)(1) which states that in establishing numeric criteria, states may adopt modified criteria based on site-specific conditions.

Current application of Technology-Based pH Limitations

Current TCEQ practice is to set pH limits of 6.0 to 9.0 s.u. based on federal secondary treatment standards for wastewater treatment facilities [40 *Code of Federal Regulations* (CFR) Part 133.102]. These technology-based effluent limitations have been consistently applied within municipal wastewater discharge permits.

Technology-based pH limitations for industrial dischargers are applied based upon the applicable federal Effluent Limitation Guideline (ELGs). In the absence of promulgated ELGs for a particular industrial/manufacturing process, pH effluent limits of 6.0 to 9.0 s.u. have typically been applied to industrial wastewater discharges based on best professional judgment (BPJ). TCEQ submits that this current practice is a more conservative approach than allowing consideration of a mixing zone. In the absence of technology-based guidelines, a mixing zone approach for pH may authorize the discharge of pH effluent levels outside of the 6.0 to 9.0 s.u. range at the point of discharge.

Comparison of Technology-Based pH limits and TSWQS pH Criteria

<u>pH Permit Limitation</u>	<u>pH Segment Criteria</u>	<u>Magnitude of Variation</u>
6.0 to 9.0 s.u.	5.5 to 9.0 s.u.	Technology-based limit is protective of segment criterion
6.0 to 9.0 s.u.	5.5 to 8.5 s.u.	0.5 s.u. difference possible at upper end of range
6.0 to 9.0 s.u.	5.5 to 8.0 s.u.	1.0 s.u. difference possible at upper end of range
6.0 to 9.0 s.u.	6.0 to 9.5 s.u.	Technology-based limit is protective of segment criterion
6.0 to 9.0 s.u.	6.0 to 9.0 s.u.	Technology-based limit is protective of segment criterion
6.0 to 9.0 s.u.	6.0 to 8.5 s.u.	0.5 s.u. difference possible at upper end of range
6.0 to 9.0 s.u.	6.5 to 9.0 s.u.	0.5 s.u. difference possible at lower end of range

Proposal for evaluating pH limit compliance with TSWQS

As noted within the above examples, segment pH criterion (listed within Appendix A of the TSWQS) vary in range from a minimum of 5.5 s.u. to a maximum of 9.5 s.u. TCEQ proposes the following evaluation procedure to clarify that permitted pH levels are protective of varying segment criterion.

1. TPDES Minor Domestic and General Permits

Permits for EPA designated minor facilities (< 1.0 MGD flow) and General Permits will require end-of-pipe compliance with technology-based limits of 6.0 to 9.0 s.u. This technology-based approach reasonably assures instream compliance with TSWQS criterion due to the relatively smaller discharge volumes authorized by these authorizations. This conservative assumption is based on TCEQ sampling conducted throughout the state which indicates that instream buffering quickly restores pH levels to ambient conditions. Similarly, this approach has been historically applied within EPA issued NPDES general permits where technology-based pH limits were established to be protective of water quality criteria.

2. TPDES Major Domestic and Industrial Permits

Texas state water quality standards allow consideration of the mixing of effluent and receiving water when conducting reasonable potential analysis and calculating water quality-based limits. Therefore, segment specific TSWQS criterion for pH does not have to be met within the mixing zone. Using a MZ approach, the discharge is required to meet the water quality standard criterion for pH at the edge of the chronic mixing zone.

TCEQ proposes to conduct an evaluation for pH as outlined within **Attachment A** of this document. For freshwater, this analysis shall generally follow the procedure in EPA's DESCONE program (*Technical Guidance on Supplementary Stream Design Conditions for Steady State Modeling*, USEPA Office of Water, Washington D.C., 1988). For saltwater, this analysis shall generally follow the procedure for calculation of pH of a mixture in seawater based on the CO2SYS program (Lewis and Wallace, 1998, <http://cdiac.esd.ornl.gov/oceans/co2rprt.html>).

If the evaluation determines that a discharge within the 6.0 to 9.0 s.u. range exceeds the applicable TSWQS pH criterion at the edge of the mixing zone, the draft permit will include the applicable TSWQS Segment pH criterion as the end-of-pipe permit limitation.

A site-specific pH mixing zone and/or alternate mixing zone model may be proposed by an applicant and considered on a case by case basis. These analyses may include effluent percentages from the Critical Conditions memorandum or site specific mixing zone modeling for the determination of effluent percentages where appropriate. If approved by TCEQ, the dimensions of the site specific pH mixing zone will be specified within the TPDES permit and the Fact Sheet will include the justification for the pH mixing zone.

3. Discharges to Unclassified Waters

All discharges to intermittent streams shall meet the technology based limitation of 6.0 to 9.0 to be protective of corresponding minimal aquatic life uses within the unclassified waterbody.

All discharges to intermittent streams with perennial pools shall meet the technology based limitation of 6.0 to 9.0 to be protective of corresponding limited aquatic life uses within the unclassified waterbody.

Continuous pH Monitoring

TCEQ will continue to restrict excursions of continuously monitored pH in accordance with the requirements of 40 CFR Part 401.17.

Attachment A pH Evaluation Procedure

TPDES Domestic Majors and Industrial Dischargers

The following evaluation procedure is based upon EPA's DESCONE program (*Technical Guidance on Supplementary Stream Design Conditions for Steady State Modeling*, USEPA Office of Water, Washington D.C., 1988)

1. Variable 1: Dilution Factor
Determine the percentage of effluent at the edge of the chronic mixing zone boundary in accordance with the Procedures to Implement the Water Quality Standards (IPs). This is provided within the Critical Conditions Interoffice Memorandum. Enter the reciprocal of the percentage of effluent at the mixing zone boundary as the dilution factor.

2. Variables 2, 3, and 4: Ambient Stream Characteristics
Input ambient Segment values for temperature, pH, and alkalinity. Site specific receiving water data shall be used when available or may be collected in accordance with the procedures outlined within the IPs. For temperature, the reviewer may input data from the nearest downstream monitoring station or the daily maximum criteria for the applicable segment within Appendix A of 30 TAC 307.

3. Variables 5, 6, and 7: Effluent Characteristics
Input effluent analysis values for temperature, pH, and alkalinity. Data may be obtained from TPDES application, the applicant, or discharge monitoring reports, as available.

The spreadsheet calculates the instream pH at the chronic mixing zone boundary.

Example A: The City of XYZ discharges treated domestic wastewater subject to technology based limitations of 6.0 to 9.0 s.u. The discharge volume is into a perennial stream greater than 300 feet prior to entering Segment No 1414 of the Colorado River Basin. The TSWQS pH criterion for Segment No. 1414 is 6.5 to 9.0 s.u. The calculated percent effluent at the edge of the chronic mixing zone is 20%.

1. Dilution Factor = $1 \div 0.20$
= 5

2. Ambient Stream Temperature = 91°F
Convert 91 °F to °C =
 $^{\circ}\text{C} = (5/9) \times (^{\circ}\text{F} - 32)$
 $^{\circ}\text{C} = (0.555) \times (91 - 32)$
 $^{\circ}\text{C} = (0.555) \times (59)$
 $^{\circ}\text{C} = 33$

3. Ambient Stream pH (Table 5 of IPs)
= 8.0 s.u.

4. Ambient Stream Alkalinity (Table 5 of IPs)
= 184 mg/L CaCO₃

5. Effluent Temperature = 88 °F
 $^{\circ}\text{C} = (5/9) \times (^{\circ}\text{F} - 32)$
 $^{\circ}\text{C} = (0.555) \times (88 - 32)$
 $^{\circ}\text{C} = (0.555) \times (56)$
 $^{\circ}\text{C} = 31$

6. Effluent pH
Use 6.0 as lower
Use 9.0 as upper

7. Effluent Alkalinity (CaCO₃)
= 150 mg/L

Run calculations twice, once using 6.0 as the lower effluent level pH and once using 9.0 s.u. as the upper effluent level pH. If the calculated values remain within the Segment No. 1414 criterion of 6.5 to 9.0 s.u., the technology based limit of 6.0 to 9.0 s.u. is protective of the criterion and will be included the draft permit . If the calculated values exceed the upper or lower bounds of the TSWQS pH criterion for Segment No. 1414, the draft permit shall include the TSWQS criterion of 6.5 to 9.0 s.u.

Example B: LMNOP Corporation discharges treated process wastewater subject to federal effluent guidelines which do not require technology based limitations for pH. The discharge volume is into a perennial stream greater than 300 feet prior to entering Segment No 1414 of the Colorado River Basin. The TSWQS pH criterion for Segment No. 1414 is 6.5 to 9.0 s.u. The calculated percent effluent at the edge of the chronic mixing zone is 20%.

1. Dilution Factor = $1 \div 0.2$
= 5

2. Ambient Stream Temperature = 91°F
Convert 91 °F to °C =
 $^{\circ}\text{C} = (5/9) \times (^{\circ}\text{F} - 32)$
 $^{\circ}\text{C} = (0.555) \times (91 - 32)$
 $^{\circ}\text{C} = (0.555) \times (59)$
 $^{\circ}\text{C} = 33$

3. Ambient Stream pH (Table 5 of IPs)
= 8.0 s.u.

4. Ambient Stream Alkalinity (Table 5 of IPs)
= 184 mg/L CaCO₃

5. Effluent Temperature = 88 °F
 $^{\circ}\text{C} = (5/9) \times (^{\circ}\text{F} - 32)$
 $^{\circ}\text{C} = (0.555) \times (88 - 32)$
 $^{\circ}\text{C} = (0.555) \times (56)$
 $^{\circ}\text{C} = 31$

6. Effluent pH
= 5.7 s.u.

7. Effluent Alkalinity (CaCO₃)
= 120 mg/L

Run calculation once using the pH effluent value reported within the permit application. If the calculated values remain within the Segment No. 1414 criterion of 6.5 to 9.0 s.u., the technology based limit of 6.0 to 9.0 s.u. is protective of the criterion and will be included the draft permit . If the calculated values exceed the upper or lower bounds of the TSWQS pH criterion for Segment No. 1414, the draft permit shall include the TSWQS criterion of 6.5 to 9.0 s.u.