STANDARD OPERATING PROCEDURE (SOP)

Title: *In Situ* Analysis of Electrical Conductivity and Water Temperature and Estimation of Total Dissolved Solids in Ambient Surface Water for the Lower Rio Grande Environmental Monitoring and Response System Using Hydrolab-Hydrotech Compact Minisondes

Team Leader: _____ Date: 3/19/19

Quality Control Officer: _____ Date: 3/22/19

Section Manager: _____ Date: 4/1/2019

Program Manager: _____ Date: 3/18/2019

Region 15 Director: _____ Date: 3/15/19

Effective Date: 4/1/2019

1.0 PURPOSE

This procedure is intended for use in the Texas Commission on Environmental Quality (TCEQ) Continuous Water Quality Monitoring Network (CWQMN) Lower Rio Grande Environmental Monitoring and Response System (EMRS) project. Continuous Ambient Monitoring Stations (CAMSs) are located at various locations on the LRG. When estimated TDS concentrations exceed the EMRS notification-level at a given station, email notifications are automatically sent to established Listservs. This procedure is designed to provide monthly service to the LRG stations to confirm proper operation and, to the extent possible, ensure that the stations are producing data at the completion of the service.

2.0 SCOPE AND APPLICABILITY

2.1 These procedures are intended for use in the Texas Commission on Environmental Quality (TCEQ) LRG CWQMN project.

2.2 EC measurements are temperature-corrected to 25.0 degrees Celsius (°C) and are reported as specific conductance (SC).

2.3 Total Dissolved Solids (TDS) in milligrams/liter (mg/L) are estimated and reported by multiplying SC in micro-Siemens/Centimeter (µS/cm) by TCEQ's statewide correction factor of 0.65.

2.4 This procedure is designed to provide monthly service to the LRG stations to confirm proper operation and to the extent possible, ensure that the stations are producing data at the completion of the service. The stations are serviced at an approximate 30 calendar day interval. Inclement weather, border security and other conditions may preclude a 30-day return interval. In such cases, service will be conducted as soon as it can be reasonably scheduled. Station service is conducted by Region 15 SWQM staff members during the first and second months of each quarter of the State Fiscal Year. TCEQ Central Office Surface Water Quality

Monitoring (SWQM) staff members conduct station service during the third month of each quarter of the State Fiscal Year.

2.5 Multi-probe sensor and deployment tube fouling is not measured as part of this procedure.

2.6 Leading Environmental Analysis and Display System (LEADS) data records for the stations are not validated. Multi-probe sensor fouling measurements are not required.

2.7 The working ranges of the sensors are listed in Table 1.

Table 1

Parameter	Working Ranges
SC	0 – 2,000 µS/cm
Water Temperature	-5 to 50 (°C)

3.0 METHOD SUMMARY

3.1 During the first and second months of each State Fiscal Year Quarter, TCEQ Region 15 SWQM staff will conduct routine maintenance at the LRG CWQMN stations. During the third month of each State Fiscal Year Quarter, TCEQ Central Office SWQM staff will conduct routine maintenance at the LRG CWQMN stations. This schedule may be modified to accommodate other Agency priorities.

3.2 Multi-probes are deployed at various locations on the LRG via deployment structures. Discrete *in situ* SC and temperature measurements are collected every 15 minutes by a data logger and the data are transmitted every 15 minutes to TCEQ's Leading Environmental Analysis and Display computer system (LEADS) in Austin, Texas.

3.3 When instantaneous in-stream SC values exceed the 1537 µS/cm (estimated 999 mg/l TDS) trigger level at a given station, LEADS automatically sends email notifications to established Listservs.

3.4 The multi-probe utilizes a Hydrolab conductivity sensor. EC measurements are based on Standard Method 2510B. The sensor is an open flow cell with four auto-ranging graphite electrodes.

3.5 Surface water temperature is measured by a resistance thermistor.

3.6 EC is converted to SC by correcting electrical conductivity to ambient water temperature.

4.0 LIMITATIONS

4.1 Multi-probe deployment structures can be susceptible to damage due to high water events and stream bank collapses. Deployment structure replacement can be expensive and require significant resources. Data collection can be interrupted due to telemetry, multi-probe, and station component problems. Station service visits may be required to fix these problems.

4.2 Over deployment periods, the interface between measurement sensors and the environment can become fouled by a variety of organisms, sedimentation, and calcification. Sensor fouling can compromise data quality. Sensor fouling generally causes SC measurements to be biased low in the LRG. However, there have been some instances where fouling has caused measurements to be biased high. When sensors become fouled with sediment, sensors can be unresponsive to changes in water quality. Over a 30-day deployment periods at the stations, sensor fouling severity can range from minimal to severe depending on station location and stream conditions. Falling stream stage conditions and associated reduction in stream velocity generally cause more sediment to accumulate in the sensor, sensor guard, and deployment tubes. Collocated SC measurements using an independent multi-probe can be made to confirm a station's measurements.

4.3 Trapped air bubbles within the sensor can cause measurement errors. Trapped air bubbles generally cause measurements to be biased low.

4.4 The temperature coefficient of most waters is only approximately the same as that of standard potassium chloride (KCl) solution; the more the temperature of measurement deviates from 25.0 °C, the greater the uncertainty in applying the SC temperature correction. The temperature coefficient used in this project is 0.0191 per degree Centigrade.

4.5 TDS concentrations are estimated by using TCEQ's statewide 0.65 SC conversion factor (0.65 x SC = TDS mg/l). TDS conversion factors vary depending on the soluble components of the water.

4.6 Monitoring station locations in the LRG are not being assessed for potential stream cross-section SC variability due to border security concerns.

4.7 Errors in SC measurements can result from inaccurate temperature measurements.

5.0 SAFETY

Border Security and associated employee safety concerns must be considered when implementing this procedure.

5.1 Not less than five (5) working days prior to LRG CWQMN field activities, the TCEQ Central Office SWQM Trip Leader or the Region 15 Trip Leader will prepare and distribute an email notification of pending field activities in Cameron, Hidalgo, and Starr Counties. The notification will be distributed to the M&A Section Manager, the WQPD Director, the Homeland Security Section Coordinator, the Region 15 Director and the IBWC Realty Specialist.

5.2 Prior to employee travel to the CWQMN stations along the Rio Grande between Harlingen and Roma, TCEQ Central Office and Region 15 staff are to consult with the United States Border Patrol Tactical Operations Centers (TOC) for the respective areas of the Rio Grande before going to the CWQMN stations.

C789	Harlingen TOC	956.366.3000
C793	Weslaco TOC	956.647.8800
C796, C767	Rio Grande City TOC	956.487.1044
C736, C791, C792	McAllen TOC	956.217.3700

5.3 This procedure includes processes that can be hazardous. Therefore, before attempting this process, operators should review the TCEQ Chemical Hygiene Plan for proper equipment and procedures necessary for the safe completion of this procedure. Operators must also read and be familiar with the Safety Data Sheets for KCl. KCl solutions do not require special handling. However, safety glasses with side shields and/or splash goggles and chemical resistant gloves should be worn when handling these chemicals. KCl has the potential to be skin and eye irritants.

54 SWQM Central Office staff conform to the Monitoring and Assessment Section Safety Plan SOP and conduct monitoring consistent with the SWQM Procedures, Volume 1, Chapter 11.

5.5 Region 15 SWQM staff conform to FIELD OPERATIONS STANDARD OPERATING PROCEDURES, INVESTIGATION GUIDANCE and Region-specific guidance and conduct monitoring consistent with the SWQM Procedures, Volume 1, Chapter 11.

6.0 EQUIPMENT AND REAGENTS

6.1 Equipment

- Hydrolab-HydroTech Minisonde
- Multiprobe copper Sensor Guard
- Sensor guard copper Nekton Screen
- Hydrolab conductivity/temperature sensor
- Surveyor 4
- NX10 handheld display
- Laptop personal computer
- Calibration cable
- Flying lead/RS232/Power cable

- Multi-probe deployment structure
- Ring stand and clamp
- Control Company Model 4000 or equivalent NIST traceable thermistor
- Instrument shelter
- Sutron datalogger
- Sutron Line of Sight radio
- Solar controller
- Solar panel
- Storage battery
- Wireless Internet Protocol modem
- Multi-probe calibration cup
- Vessel for multi-probe temperature sensor checks
- Instrument log book
- YSI C-spray anti-fouling nano-polymer

6.2 Standards and Reagents (All reagents/chemicals must be analytical reagent grade).

- KCl conductivity calibration solutions (2,000 µ S/cm) traceable to National Institute of Standards and Technology (NIST). Expired KCl standards must not be used for calibrations or calibration verifications.
- Thermistor or thermometer certified or traceable to NIST with 0.1°C resolution. Thermistor must be recertified every two years.
- De-ionized (DI) water

6.3 Multi-probe and Deployment Tube Cleaning Supplies.

- Chimney brush polypropylene approximately 4" in diameter and extensions
- Five-gallon bucket
- Paper towels
- All-purpose cleaner
- Medium soft-bristle brush
- Small soft-bristle brush
- Cotton swabs and isopropyl alcohol to clean conductivity sensor orifice
- White vinegar for cleaning sensor hard fouling

6.4 Project Forms

- LRG HYDROLAB-HYDROTECH CALIBRATION WORKSHEET (Appendix A)
- LRG STATION SERVICE WORKSHEET (Appendix B)

7.0 PROCEDURE

Multi-probe sondes are continuously deployed at various locations on the LRG via poly vinyl chloride (PVC) deployment tubes. Every business day, each station's water quality parameters are monitored remotely by Water Quality Planning Division (WQPD) staff to evaluate the general operational status of the stations. Stations are serviced approximately every 30 calendar days. Station service

includes multi-probe conductivity sensor calibration, multi-probe temperature sensor verification, deployment tube cleaning, newly calibrated multi-probe deployment, and operator log entry.

7.1 Station Monitoring – Daily Data Review Report

Every business day, WQPD staff remotely monitors the general operational status of all stations in the LRG and emails a daily report to interested parties. If problems are identified, a station visit may be needed to correct problems. The report contains the following information.

- Stations on-line
- Stations reporting data
- Reasonableness of the data
- Data concerns
- Other comments

7.2 Multi-probe Sonde Deployment

Multi-probes are deployed via PVC deployment tubes. The PVC tube is deployed at a fixed point in the water body. Deployment tubes include 48 evenly spaced 1-inch diameter holes per linear foot for at least the lower two feet of the deployment tube to allow water to flow across the sensors.

7.3 C-Spray Anti - Fouling Application

Prior to multi-probe calibration, two coats of C-spray nano-polymer must be applied to the multi-probe. Ensure entire multi-probe, EC sensor bodies, and sensors interfaces are clean and dry. Apply C-spray to sonde body, multi-probe, conductivity sensors, and allow to air dry. Apply a second coat of C-spray and allow to air dry.

7.4 General Calibration Procedure

Multi-probe sensors must be calibrated prior to multi-probe deployments in a laboratory or other controlled environment.

- Multi-probe sonde and sensors must be clean prior to calibration.
- Multi-probe SC sensors should be calibrated in the laboratory close to 25 °C as possible. However, there can be rare circumstances when multi-probes need to be calibrated in the field. When this occurs, the multi-probe's temperature sensor check will not occur.
- Prior to multi-probe calibration, two coats of C-spray nano-polymer must be applied to the multi-probe.
- The multi-probe temperature sensor must be checked prior to SC sensor calibration.

- Before the SC sensor is calibrated, the sensor's zero reading must be checked in ambient air. SC measurements must be ≤ 3 µS/cm.
- Conductivity standards must be within expiration date.
- SC sensors must be rinsed twice with DI or distilled water before sensors are pre-rinsed with KCl standards.
- Slowly fill calibration cup with standard to minimize air bubbles. Ensure sensors are immersed in KCl calibration solutions.
- After sensors are immersed in calibration standards, inspect the conductivity sensor interface for air bubbles. Air bubbles will cause a lower sensor response. If air bubbles are observed, re-introduce standards until no bubbles are present.
- Allow sensors time to stabilize before calibration or initial readings.
- Have several clean absorbent paper towels available.

7.4.1 Single-Point SC Calibration

Calibration of the SC sensor consists of a single-point calibration with a 2,000 µS/cm KCl solution. During the calibration, the multi-probe sensor will measure the temperature of the standard and automatically calculate the SC of the standard.

7.4.1.1 Multi-probe and sensors must be cleaned prior to calibration. For further details, see section 9.2.

7.4.1.2 Two coats of C-spray must be applied to multi-probe and sensor prior to calibration. For further details, see section 9.1 (General Calibration Procedures).

7.4.1.3 The multi-probe's temperature sensor must be checked prior to calibration. For further details, see section 9.4.

7.4.1.4 Connect the multi-probe sonde via calibration cable to the Surveyor 4 and press the Surveyor 4 power button.

7.4.1.5 In ambient air, SC measurements must be ≤ 3 µ S/cm. If measurements are greater than 3 µ S/cm, redo check. If still failing, the sensor cannot be used and must be replaced with viable multi-probe that measures ≤ 3 µ S/cm in ambient air.

7.4.1.6 Rinse sensor twice with DI water and conductivity standard using the calibration cup.

7.4.1.7 Place probe in the cup, Fill the calibration cup with conductivity standard. Pour standard in slowly in order to minimize air bubbles. Make sure the conductivity and temperature sensors are completely submerged. Gently tap the side of the calibration cup

to dislodge any air bubbles from the cell. Inspect sensor interface for air bubbles. If air bubbles are still present, re-introduce standards until no air bubbles are present.

7.4.1.8 Allow time for the standard to equilibrate. After SC readings have stabilized, record initial temperature and SC readings into the LRG HYDROLAB-HYDROTECH CALIBRATION WORKSHEET (Appendix A).

7.4.1.9 Using the Surveyor 4, from the main menu, select *Setup/Cal.* Then select *Calibrate,* select *Sonde,* select *SpCond: µS/cm.* Enter "new" calibration standard value. To calibrate, select *Done*. Select *Go Back* until main menu appears and record specific conductance calibrated to measurements into the LRG HYDROLAB-HYDROTECH CALIBRATION WORKSHEET (Appendix A).

7.4.1.10 When the LRG HYDROLAB-HYDROTECH CALIBRATION WORKSHEET (Appendix A) is complete, scan the document and send an electronic copy (pdf) to the CWQMN Coordinator and the CWQMN Quality Assurance Officer. Electronic copies will be maintained on a common TCEQ server for a minimum of five (5) years.

7.5 Station Service

7.5.1 Prior to any station service event that disrupts ambient stream data collection, the station operator logs into the station datalogger and changes the parameter status to P code (preventative Maintenance mode) from "K" code (ambient sampling mode). Placing the station into P code prevents any erroneous data collected during station service events from being reported in LEADS as ambient stream data. The station operator enters an operator log on the station datalogger announcing pending station service and indicating the parameters have been placed in P code. The station operator(s) include their initials in the operator log.

7.5.2 Collect parameter readings for temperature and specific conductance from the deployed sonde and record the data on the LRG STATION SERVICE WORKSHEET (Appendix B) before removing the sonde from the deployment tube. Remove the deployed sonde and record the sonde serial number on the LRG STATION SERVICE WORKSHEET.

7.5.3 The station operator cleans the multi-probe deployment tubes with a chimney brush as part of every station service event.

7.5.4 Deploy the freshly deployed sonde and record the serial number on the LRG STATION SERVICE WORKSHEET (Appendix B). Collect and

record parameter readings for temperature and specific conductance from the deployed sonde on the data on the LRG STATION SERVICE WORKSHEET.

7.5.5 When station service is complete, the station operator places the parameters back in K code and enters an operator log indicating the completion of service and the return of parameters to K code. Operator logs must contain:

7.5.5.1 Routine Station Service Operator Log Content

- Conducted routine station service
- Note applicable field observations: water conditions, meteorological conditions, drought, flood etc.
- Operator(s) initials

7.5.5.2 Non-routine Station Service Operator Log Content

- Any problems with data collection that can affect data quality
- Change in operating procedures, data collection circumstances, or measurement equipment
- Station equipment/communication problems and any troubleshooting activities.
- Station either being taken off-line or being brought on-line
- Non-routine station service events
- Date and time (or exact time frames) of the event must be included in Operator Logs.
- Operator(s) initials.

7.5.6 When the station operator returns to the office, the LRG STATION SERVICE WORKSHEET (Appendix A) is scanned, saved to local network drive and an electronic copy of the document (pdf) is sent to the CWQMN Coordinator and the CWQMN Quality Assurance Officer. Electronic copies will be maintained on a common TCEQ server for a minimum of five (5) years by the CWQMN Coordinator.

8.0 CALCULATIONS

8.1 Sample Specific Conductance

Conductivity is reported as SC (KCl) using calculation found in Standard Method 2510B:

$$SC = \frac{AC}{1 + 0.0191 \times (t - 25.0)}$$

Where:
SC = normalized conductivity in µS/cm;
AC = actual conductivity; and
t = solution temperature in degrees C.

8.2 Total Dissolved Solids (TDS) in mg/l are estimated and reported from SC values using a conversion factor:

TDS mg/l ≈ SC x 0.65

8.3 Measurement accuracy of the temperature sensor can be expressed in terms of the absolute error (AE) and is defined as:

$$AE = Measured\,Value - Actual\,Value$$

The Relative Percent Error (RPE) of the specific conductance is a measure of the magnitude of the error and is defined as:

$$RPE = \frac{Measured\,Value - Actual\,Value}{Actual\,Value} * 100$$

Where the Measured Value is the value from the deployed multi-probe before the deployment tube and multi-probe are disturbed and the Actual Value is the value of the freshly calibrated multi-probe after the deployment tube is cleaned.

9.0 Quality Control

9.1 Quality Control

Quality control consists of ensuring multi-probe sondes are operational when deployed and station deployment tubes are cleaned prior to multi-probe deployments. Before station service and after station service, multi-probe temperature and SC measurements are collected to provide information on the (RPE) between the previously deployed and the newly deployed sonde.

9.2 Multi-probe and Deployment Tube Cleaning Procedures

Multi-probe sondes and sensors must be cleaned during station service events when multi-probe sondes are exchanged to prevent hardening of deposits on the instruments. Multi-probe cleaning includes the thorough cleaning of the sensor interface, sensor body, sensor guard, nekton screen, and multi-probe body using cleaning supplies listed in Section 6.3. Deployment tubes must be cleaned as part of every routine station service event.

9.2.1 Spray entire multi-probe, sensor bodies, sensor guard, nekton screen, and sensor interfaces with all-purpose cleaning solution.

9.2.2 Clean all components using the medium and small soft-bristle brushes in a five-gallon bucket.

9.2.3 After cleaning using the sonde with all-purpose cleaning solution, clean the conductivity sensor cell (orifice) using cotton swabs and isopropyl alcohol.

9.2.4 Rinse multi-probe, sensor bodies, and conductivity sensor interface. Inspect multi-probe (especially sensor interface) and repeat steps 9.2.1 - 9.2.3, if necessary.

9.2.5 Thoroughly clean deployment tube using the chimney brush.

9.3 Before and After Station Service Multi-Probe Measurements

Before station service and after station service, multi-probe temperature and SC measurements are collected.

9.3.1 Without disturbing the deployed multi-probe, collect temperature and SC measurements from the deployed multi-probe via the Sutron data logger. Record results in the LRG STATION SERVICE WORKSHEET (Appendix B).

9.3.2 After the deployment tube is cleaned and the new clean and calibrated multi-probe is deployed, collect temperature and SC measurements from the multi-probe via the Sutron data logger. Record results in the LRG STATION SERVICE WORKSHEET (Appendix B).

9.4 Multi-probe Temperature Sensor Check

9.4.1 In a temperature-controlled environment, fill a vessel with water and immerse the Hydrolab-HydroTech multi-probe temperature sensor. Allow the sensor time to stabilize. Place the end of the NIST traceable thermistor thermocouple next to the multi-probe temperature sensor (allow the measuring device time to stabilize). The multi-probe temperature measurement must be within ± 0.50°C of the NIST certified or traceable thermistor. Record results into the LRG HYDROLAB-HYDROTECH CALIBRATION WORKSHEET (Appendix A).

9.4.1 I f the multi-probe temperature measurement is not within ± 0.50°C of the NIST certified or traceable thermistor, the sensor and sonde cannot be deployed until remedial action corrects the condition and an acceptable

measurement is observed.

Table 9-1: Multi-probe QC Checks

QC Check	Purpose	Frequency	Acceptance Criteria	Response Action
Temperature sensor check	To assess thermistor accuracy	Prior to SC sensor calibration	± 0.50 °C	1) Perform corrective action as necessary 2) Replace multi-probe
SC sensor zero check in ambient air	To assess SC zero	Prior to or after SC sensor single-point calibration	Initial zero reading is ≤3 µS/cm	1) Perform corrective action as necessary 2) Replace multi-probe
Single-point SC calibration	To establish slope used for quantitation	Prior to multi-probe deployments.	Instrument accepts calibration.	1) Perform corrective action as necessary 2) Replace multi-probe
Before and after station service multi-probe measurements	Provide information on sensor/deployment tube fouling	Monthly Station Service Events.	None (RPE)	1) Clean sensors / deployment tube on a more frequent basis

10.0 DEFINITIONS

See Appendix A of the current TCEQ *Continuous Water Quality Monitoring Quality Assurance Project Plan.*

11.0 REFERENCES

TCEQ *Continuous Water Quality Monitoring Network Quality Assurance Project Plan*
Hydrolab *User Manual Edition 1*
HydroLab *Surveyor 4a User Manual Edition 2*
HACH/Hydromet *Custom Report for TCEQ 10/4/11, Hydrolab Conductivity Temperature Compensation*
TCEQ *Surface Water Quality Monitoring Procedures, Volume I*
TCEQ *Operating Policies and Procedures, Chapter 6.13*
TCEQ *Field Operations Standard Operating Procedures, Investigation Guidance and*

TCEQ Office of Compliance and Enforcement *Region-specific guidance*
TCEQ *SWQM Monitoring and Assessment Safety Plan SOP*

12.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

Supervisors, sampling personnel, and laboratory analysts should identify and implement innovative and cost-saving waste reduction procedures as part of the method development, review, and revision of standard operating procedures. Wastes that do result from these procedures are managed and disposed of in accordance with appropriate state and federal regulations.

Refer to Chapter 6.13 of the *TCEQ Operating Policies and Procedures* for guidelines on general recycling, waste reduction, and water and energy conservation. Review these procedures for specific employee responsibilities and mechanisms for office-related waste prevention and management. Consult the *Monitoring Operations Hazardous Waste Disposal Plan* for laboratory-specific waste minimization recommendations and requirements for proper handling of hazardous waste resulting from laboratory procedures.

The reagents, washes, standards, and waste associated with this procedure do not require special disposal. Before disposing waste into a municipal sewer system, check with respective municipal sewer system on what concentration levels can be put into their system.

Appendix A

LRG HYDROLAB-HYDROTECH CALIBRATION WORKSHEET					
Analyst:			Calibration Date/Time:		
Multi-probe Serial Number:					
Standard	**Manufacturer**		**Lot No.**		**Expiration Date**
Conductivity					
Temperature Sensor Check	**NIST Thermometer Reading**		**Sensor Response**	**Difference**	**Criterion**
					± 0.50 degrees C°
Parameter	**Temp. of Standard**	**SC of Calibration Standard**	**Initial Reading or Zero reading**	**Calibrated to**	**Criterion/Comments**
Zero SC (µS/cm)		Ambient Air			Zero must be ≤ 3 µS/cm
Full Scale SC (µS/cm)		2,000 µS/cm			

Comments:

Appendix A

LRG STATION SERVICE WORKSHEET

SITE OPERATOR(S): _____

DEPLOYED HYDROLAB-HYDROTECH MINISONDE SN: _____

RETRIEVED HYDROLAB-HYDROTECH MINISONDE SN: _____

DATE: _____

DEPLOYMENT TUBE CLEANED? _____

TIME: _____

MULTI-PROBE AND SENSORS CLEANED? _____

CAMS NUMBER: _____

	Multi-probe S/N	Temp (C°)	SC (µS/cm)
Before Service			
After Service			
	Results	AE	RPE

Comments: