February 2016 – August 2017

QUALITY ASSURANCE PROJECT PLAN FOR THE EVALUATION OF CONTINUOUS WATER QUALITY MONITORING NUTRIENT ANALYZERS

EPA FEDERAL GRANT # I-98662308

Water Quality Planning Division

TEXAS COMMISSION ON ENVIRONMENTAL QUALITY

QUALITY ASSURANCE PROJECT PLAN FOR THE EVALUATION OF CONTINUOUS WATER QUALITY MONITORING NUTRIENT ANALYZERS

Texas Institute for Applied Environmental Research
Tarleton State University
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A1 APPROVAL PAGE

12/4/2015

Charles Dvorsky
TCEQ Project Manager, TCEQ SWQM
Date

12/4/2015

Andrew Sullivan
SWQM Team Leader, TCEQ SWQM
Date

12/8/2015

Patricia Wise
Section Manager, TCEQ Monitoring & Assessment Section
Date

12/9/2015

Daniel Burke
CWQMN Quality Assurance Officer
Date

12/9/2015

Sharon R. Coleman
TCEQ Quality Assurance Manager
Date

12/4/15

Edward Ragsdale
CWQMN Quality Control Officer, TCEQ SWQM
Date

12/4/15

Cathy Anderson
Team Leader Data Management and Analysis Section
Date

A1 APPROVAL PAGE, continued

Larry Hauck
TIAER Project Manager

Date: 12 Nov 2015

Todd Adams
TIAER Site Operator

Date: 12 Nov 2015

Mark Murphy
TIAER Laboratory Manager and Laboratory QAO

Date: 11/12/15

A1 Approval Page (continued)

U.S. Environmental Protection Agency (EPA)

Teresita Mendiola
U.S. EPA 106 Project Officer
State and Tribal Programs Section
Assistance Programs Branch

2/16/16
Date

Curry Jones, M.P.H
Chief
State and Tribal Programs
Section

2/16/16
Date

A2 TABLE OF CONTENTS

LIST OF ACRONYMS

AWRL	**Ambient Water Reporting Limit**
ASTM	**American Society for Testing and Materials**
ºC	**Degrees Centigrade**
CC	**Cubic Centimeter**
CAMS	**Continuous Ambient Monitoring Station**
CAR	**Corrective Action Report**
COC	**Chain of Custody**
CWQMN	**Continuous Water Quality Monitoring Network**
DOC	**Demonstration of Capability**
DQO	**Data Quality Objective**
EPA	**Environmental Protection Agency**
ESMS	**Environmental Sample Data Management System**
FY	**Fiscal Year**
FSR	**Financial Status Report**
HCL	**Hydrochloric**
ID	**Identification**
LCS	**Laboratory Control Standard**
LCSD	**Laboratory Control Standard Duplicate**
LOQ	**Limit of Quantitation**
M	**Molar**
mg	**Milligrams**
mg/L	**Milligrams per liter**
mL	**Milliliter**
MPR	**Monthly Progress Report**
NA	**Not Applicable**
NELAP	**National Environmental Laboratory Accreditation Program**
PVC	**Polyvinyl chloride**
QA	**Quality Assurance**
QAM	**Quality Assurance Manual**
QAO	**Quality Assurance Officer**
QAPP	**Quality Assurance Project Plan**
QC	**Quality Control**
RPD	**Relative Percent Difference**
SOP	**Standard Operating Procedure**
SUNA	**Submersible Ultraviolet Nitrate Analyzer**
SWQM	**Surface Water Quality Monitoring**

TAC	**Texas Administrative Code**
TBD	**To Be Determined**
TCEQ	**Texas Commission on Environmental Quality**
TIAER	**Texas Institute for Applied Environmental Research**
TNI	**The NELAC Institute**
TSS	**Total suspended solids**
UV	**Ultra Violet**
USGS	**United States Geological Survey**
WQPD	**Water Quality Planning Division**

A3 DISTRIBUTION LIST

TEXAS COMMISSION ON ENVIRONMENTAL QUALITY CENTRAL OFFICE

Patricia Wise, Manager, Monitoring & Assessment Section, Water Quality Planning Division

Andrew Sullivan, Team Leader, Surface Water Quality Monitoring Team, Monitoring & Assessment Section, Water Quality Planning Division

Charles Dvorsky, Network Coordinator, Surface Water Quality Monitoring Team, Monitoring & Assessment Section, Water Quality Planning Division

Daniel Burke, CWQMN Quality Assurance Officer, Laboratory & Quality Assurance Section, Monitoring Division

Michele Blair, Surface Water Quality Monitoring Team, Monitoring & Assessment Section, Water Quality Planning Division

Edward Ragsdale, CWQMN Quality Control Officer, Surface Water Quality Monitoring Team, Monitoring & Assessment Section, Water Quality Planning Division

Robin Cypher, Surface Water Quality Monitoring Team, Monitoring & Assessment Section, Water Quality Planning Division

Pat Bohannon, Surface Water Quality Monitoring Team, Monitoring & Assessment Section, Water Quality Planning Division

Bill Harrison, Surface Water Quality Monitoring Team, Monitoring & Assessment Section, Water Quality Planning Division

Peter Bohls, Data Management & Analysis Team, Monitoring & Assessment Section, Water Quality Planning Division

Cathy Anderson, Team Leader, Data Management & Analysis Team, Monitoring & Assessment Section, Water Quality Planning Division

Debbie Peters, Division Support Section, Water Quality Planning Division

Texas Institute for Applied Environmental Research

Larry Hauck, Project Manager

Todd Adams, Site Operator

Mark Murphy, Laboratory Manager and Laboratory QAO

United States Environmental Protection Agency

Teresita Mendiola, U.S. EPA 106 Project Officer, State and Tribal Programs Section, Assistance Programs Branch

Curry Jones, M.P.H, Chief, State and Tribal Programs Section

QAPP Distribution

The TCEQ Project Manager will provide copies of this QAPP and any amendments or revisions of this plan to each person on the distribution list including participants other than TCEQ staff.

The TIAER Project Manager will provide documentation of this transmittal to the TCEQ Project Manager within two weeks of QAPP approval. This documentation will be maintained as part of TIAER's as part of the project file.

A4 PROJECT/TASK ORGANIZATION

This section is intended to identify TCEQ and TIAER staff responsible for developing and/or supporting this project. (See Figure A4.1 for Project Organizational Chart)

A4.1 TCEQ Project Manager, Office of Water, Monitoring & Assessment Section, Water Quality Planning Division (Charles Dvorsky)

* Provides overall project support for coordination, development, and installation of nutrient analyzers
* Purchase needed equipment for project
* Maintains training records for Cycle-P and SUNA V2
* Responsible for distribution of this QAPP to pertinent parties in TCEQ and TIAER
* Reviews QAPP

A4.2 TCEQ CWQMN QC Officer, Office of Water, Monitoring & Assessment Section, Water Quality Planning Division (Edward Ragsdale)

- Reviews QAPP

A4.3 TCEQ Implementation Team (Keith Talley)

* Provides overall support and logistics for TCEQ monitoring stations.

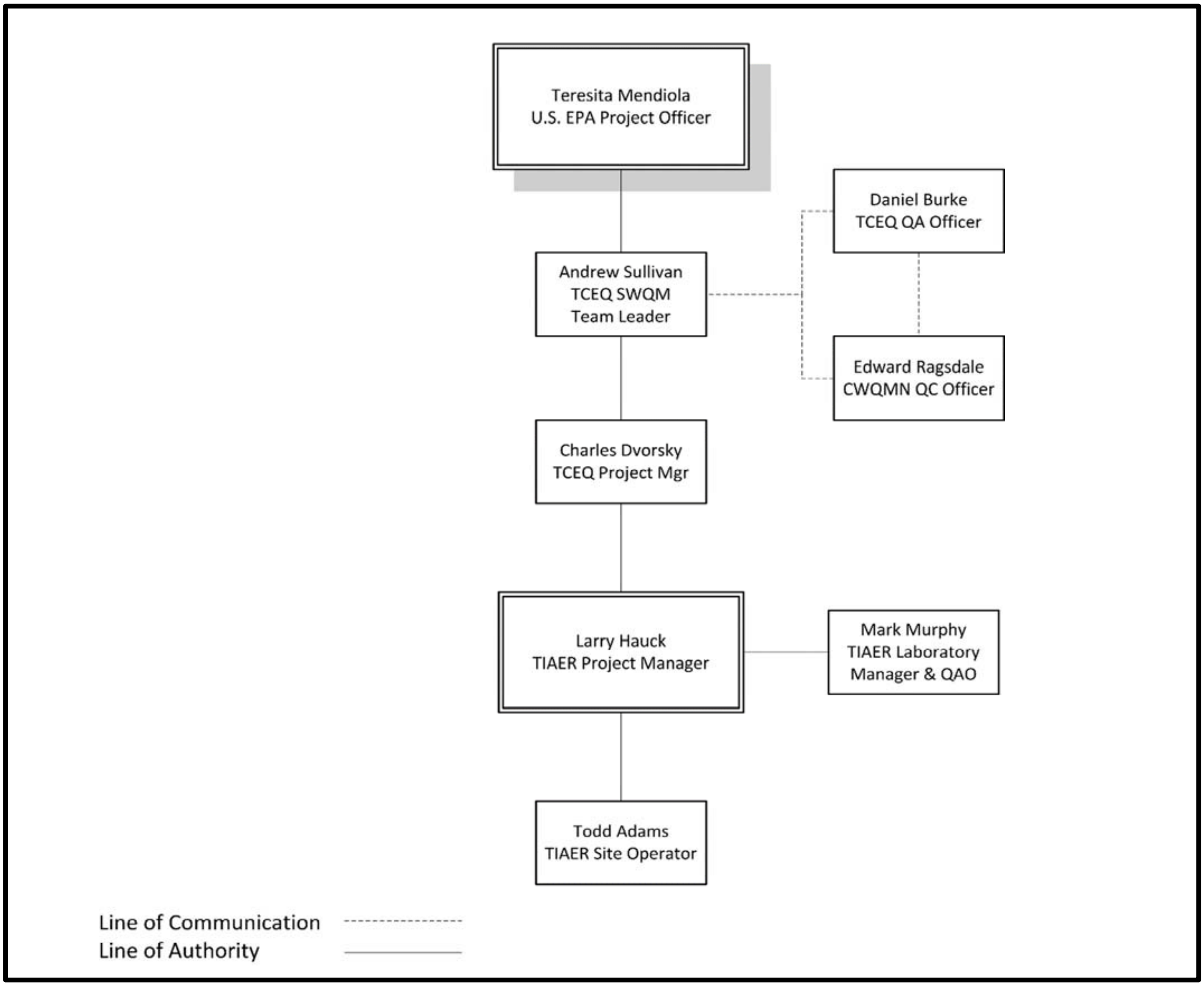
A4.4 TCEQ Implementation Team (Gary Sodergren)

* Provides overall support for the fabrication and deployment of the monitoring stations.
* Provides overall support for training to operate and maintain station infrastructure.

A4.5 TCEQ Data Collection Team (Robert Hernandez)

* Provides overall support for the fabrication and deployment of the monitoring stations.
* Provides overall support of monitoring station communication and electronic data acquisition needs and provides training on the operation of communications equipment.
* Participates in station deployments

Figure A4.1Project Organization Chart



A4.6 TCEQ Quality Assurance Officer (Daniel R. Burke)

- Provides oversight of all QA activities.
- Participates in the development, approval, implementation and maintenance of written QAPPs.
- Determines conformance with program quality system requirements.
- Provides technical expertise and/or consultation on quality services.
- Serves as quality system representative.

A4.7 TIAER Project Management (Larry Hauck)

- Serves as liaison between TIAER and TCEQ
- Responsible for distribution of this QAPP to appropriate TIAER staff

A4.8 TIAER Site Operator (Todd Adams)

- Operates and maintains the CAMS 725 station and sampling equipment and oversees TIAER support staff that assist in all operational capacities. Oversees collection of comparison grab samples. Participates in and oversees development of SOPs as specified in project Scope of Work.

A4.9 TIAER Laboratory Manager and Laboratory Quality Assurance Officer (Mark Murphy)

- Oversees analyses of laboratory water quality samples and assures conformity to quality criteria specified in this QAPP.
- Maintains all training records for staff working in the TIAER Laboratory

A5 PROBLEM DEFINITION/BACKGROUND

<u>Project Background and Goal</u>

Since 2001, the TCEQ has been engaged in continuous water quality monitoring of designated waterbodies within the State of Texas with the development of the Continuous Water Quality Monitoring Network (CWQMN). This monitoring network has employed various monitoring equipment (sensors, analyzers, multiprobes, etc.) in both in situ and ex situ environments. In anticipation of future continuous water quality monitoring requests, the TCEQ is investigating the operational feasibility of two additional types of nutrient sensors for continuous monitoring of dissolved nitrate-plus-nitrite nitrogen and dissolved orthophosphate phosphorus. Note that the term "continuous" is employed within this document to describe a system with continuous deployment of the instrumentation at the sampling site, discrete sampling occurring at an interval not to exceed two hours (one hour will be initially prescribed for this project), providing temporal intensity of data collection not achievable in an affordable manner with other means of sampling and analysis, and by the nature of the intensity of sampling resulting in strong serial correlation of concentration readings.

These, or other instruments may subsequently be deployed to address a variety of data needs such as targeting field investigations and special studies of nutrient-rich waterbodies. The utility of the data for various purposes may be constrained by the instruments' operational range including minimum detection limits in ambient waters, minimum level of quantification in ambient waters, maximum level of quantification in ambient waters, and the ability of the instruments and methods to achieve NELAC accreditation. However, at a minimum, the instruments are expected to generate data of sufficient quality to target field investigations of unpermitted wastewater discharges.

The TCEQ has contracted with TIAER to evaluate and document operating procedures for the SUNA V2 nitrite plus nitrate sensor and Cycle-P orthophosphate analyzers at one continuous water quality monitoring station (CAMS 725) in the North Bosque River watershed. Both instruments are manufactured by Sea-Bird Coastal and employ optical-based nutrient sensing technologies that are designed for in- stream applications and are considered to be more cost-effective than other in stream nutrient monitoring systems. The SUNA V2 utilizes ultra violet spectrometry to measure nitrite and nitrate absorption and, thus operates free of standards and reagents. The Cycle-P analyzer employs optical colorimetric methodology (based on EPA method 365.5) to measure dissolved orthophosphate phosphorus concentrations.

For this project, TIAER will operate and maintain the SUNA V2 nitrite plus nitrate sensor and the Cycle-P orthophosphate analyzer in a flow-thru, ex situ sampling system; test the results of the instruments against laboratory results for comparison grab samples, and develop and maintain standard operating procedures for both instruments.

The Project Scope of Work is provided as Appendix A.

A6 PROJECT/TASK DESCRIPTION

This QAPP provides specifications for evaluating the two nutrient sensors for future continuous water quality monitoring purposes at an existing monitoring station in the North Bosque River watershed. The monitoring station, CAMS 725, is located on the North Bosque River at State Highway 6, near Clairette, Texas. Figure A6.1 presents the station location and drainage area for the station.

A CAMS trailer is located on a bridge in close proximity to the waterbody at CAMS 725. The two instruments, a Sutron data logger, and other peripheral equipment will be installed in the trailer and incorporated with a sample delivery system consisting of an 8-inch diameter PVC tube with an intake line originating in the waterbody. Figure A6.2 presents the sample delivery system and monitoring system design.

Discrete measurements will be collected at intervals to be determined, but may be as frequent as hourly, by a Sutron data logger. Data will be reviewed weekly, except during holidays or inclement weather events, by TIAER staff to determine whether the sensors are functioning properly and providing data that are reasonable.

TIAER will also test the results of the SUNA V2 nitrite plus nitrate sensor and the Cycle-P orthophosphate analyzer against laboratory results for comparison grab samples, which will be performed on a periodic basis.

Figure A6.1 Station CAMS 725 Location and Watershed Area

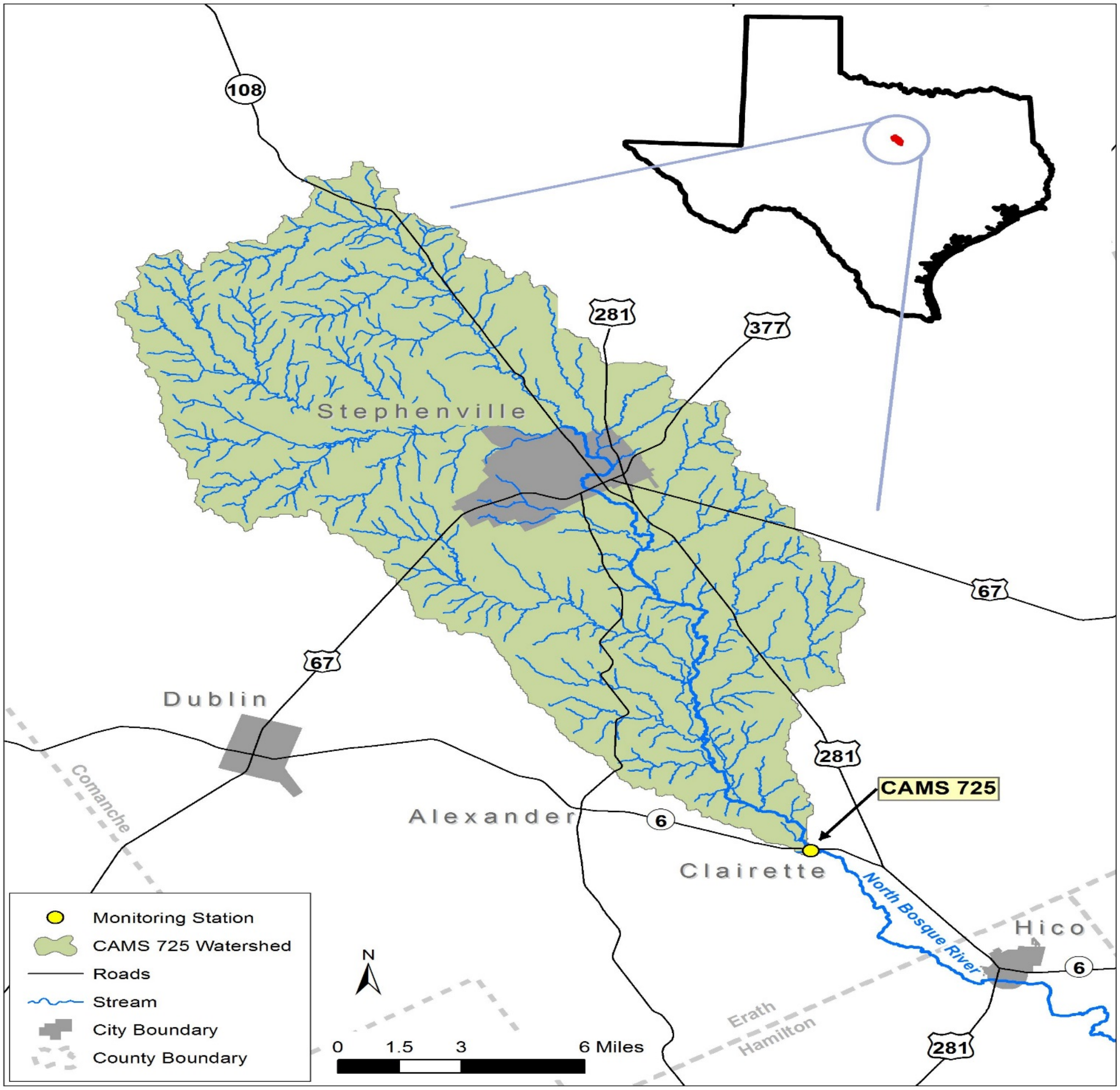
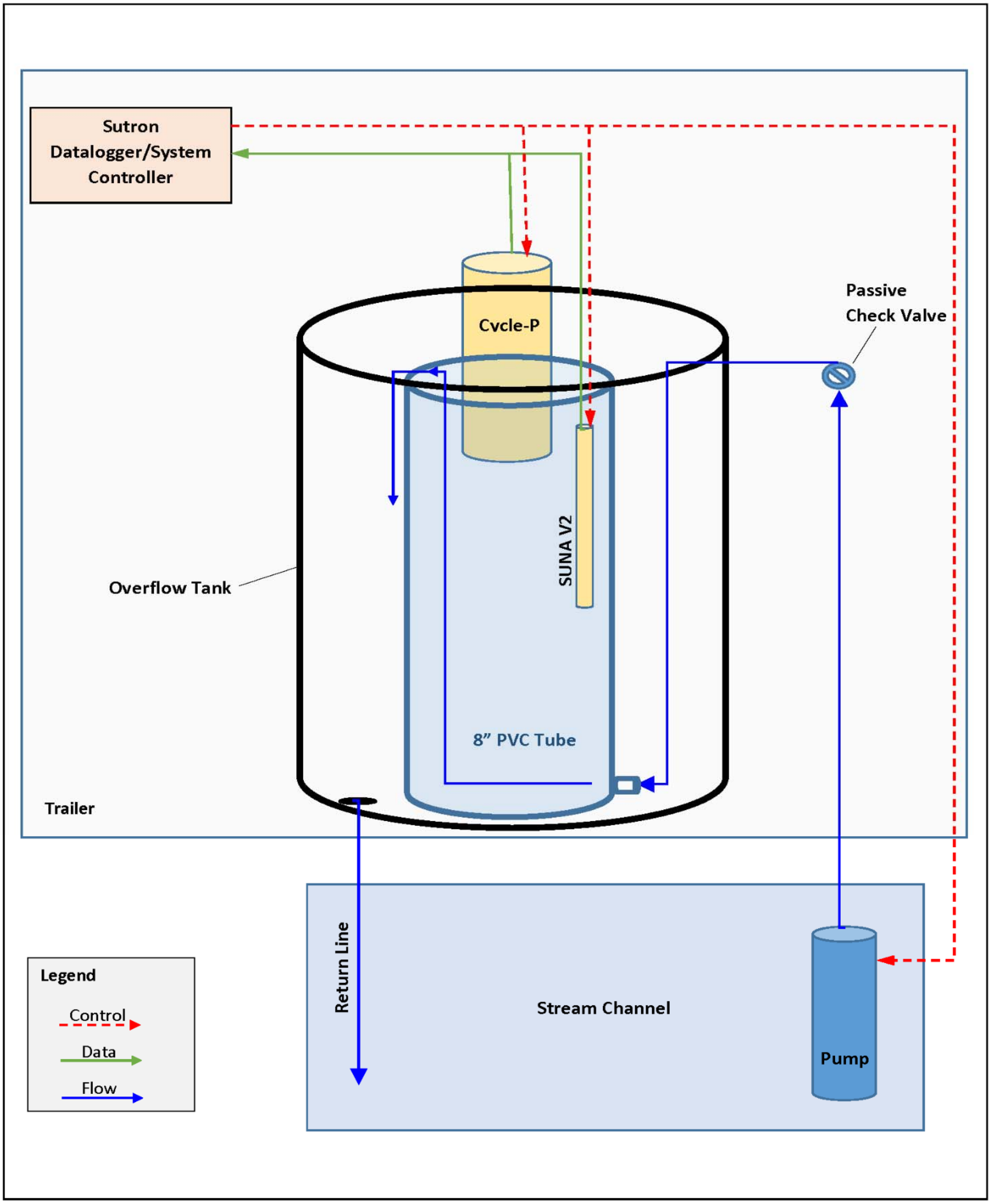


Figure A6.2 CAMS 725 Sample Delivery System and Monitoring System Design Diagram



A7 QUALITY OBJECTIVES AND CRITERIA

SUNA V2 and Cycle-P Quality Objectives

The goal of this project is to operate and evaluate the SUNA V2 sensor and Cycle-P nutrient analyzer installed at the CAMS 725 station and to develop standard operating procedures (SOPs) for the two instruments. Due to the experimental nature of this project, data records from this project will not be validated for production or public decision dissemination. Furthermore, because the operation of both instruments and station development is an on-going effort, additional quality objectives and criteria may be discovered over the course of the project and will be implemented as discovered. Table A7.1 summarizes the project's known quality objectives for the SUNA V2 and Cycle-P, which will be used to develop the project/instrument-specific SOPs, as referenced in Appendix A, Project Scope of Work. Table A7.2 summarizes manufacturer's specifications for the SUNA V2 sensor and Cycle-P nutrient analyzer.

Representativeness

By design the SUNA V2 and Cycle-P installation measures water quality in greater temporal detail and resolution than is possible with grab samples and short term deployments of instruments providing an improvement in representativeness of environmental conditions over traditional monitoring methods. As described in greater detail in Sections B1 and B2, the intake to bring water samples is located to avoid excessive vegetation and backwater areas that provide non-representative areas for monitoring. An additional measure of representativeness is maintained by sampling while the water intake pump is activated providing flowing water to the instruments.

Comparability

CWQMN water quality measurements are based on *Standard Methods for the Examination of Water and Wastewater* (Standard Methods, 2016), latest online edition, unless otherwise noted.

Comparability will also be achieved by using SOPs that are being developed as part of this project, reporting data in standard units by using accepted rules for significant figures, and by reporting data in standard formats.

Completeness

There are no criteria for data completeness for the SUNA V2 and Cycle-P instruments. Data completeness for the laboratory aspects of this project are described in the "Completeness" paragraph in the TIAER Laboratory Quality Objectives for Comparison Samples section on page 16.

Table A7.1
Station Monitoring, SUNA V2 and Cycle-P Quality Control, Criteria, and Response Actions

Quality Control	Purpose	Frequency	Acceptance Criteria	Response Action
Monitor Operational Status of the Stations	To ensure stations are operational	TBD	Station is reporting measurement data; data appear reasonable	Determine and perform corrective action
Sensor Cleaning	To maintain equipment sensitivity	As needed and/or per manufacturer recommendations	None	Clean sensors as frequently as needed
Sensor specific baseline check counts (Cycle-P only)	To assess interference from optical window staining	Before each sampling event	>499 counts	Perform manufacturer's optical window cleaning procedure.
Reference Spectra Update (SUNA V2 only)	To address interference	TBD	TBD	Perform manufacturer's update procedure
Integrated Sensor Wiper (SUNA V2 only)	To address biofouling	Before each sampling event	None	Determine and perform corrective action
Comparison of results to laboratory analyses	To determine reliability of results	Once every two weeks for 1 year, supplemented with biased sampling	None	Determine situational and conditional limitations

Table A7.2
Quality Objectives SUNA V2 and Cycle-P from Manufactures Specifications

Parameter	SOP	MDL	AWRL	Precision
OPO_4-P (Cycle-P)	Project to develop SOPs	0.0077	0.04 mg/L	±0.006 mg/L for concentrations of 0.016-0.15 mg/L
Total NO_2-+NO_3-N (SUNA V2)	Project to develop SOPs	0.007 mg/L	0.05 mg/L	Greater of ±10 % of reading or ±0.028 mg/L

TIAER Laboratory Quality Objectives for Comparison Grab Samples

Table A7.3 lists analytes measured in the TIAER Laboratory for this project, with TCEQ parameter codes, units, analytical methods, and measurement performance specifications.

Table A7.3
Project Laboratory Analytes and Measurement Performance Specifications

Parameter	Units	Method	Parameter Code	AWRL	Limit of Quantitation (LOQ)	Recovery at LOQ (%)	Recovery of LCS	Precision LCS/LCSD (%RPD)
NO_2-N+NO_3-N, Nitrate/nitrite-N, total	mg-N /L	SM online 4500NO3-F	00630	0.05	0.05	70-130%	80-120%	20
OPO_4-P, Orthophosphate-P, dissolved, field filtered	mg-P /L	SM online 4500P-E	00671	0.04	0.005	70-130%	80-120%	20
OPO_4-P, Orthophosphate-P, dissolved, lab filtered	mg-P /L	SM online 4500P-E	70507	0.04	0.005	70-130%	80-120%	20
Residue, total nonfilterable (also referred to as TSS, Total Suspended Solids)	mg/L	SM online 2540D	00530	5	4	NA	80-120%	20

Reporting Limits

The Ambient Water Reporting Limit (AWRL) value for each analyte of interest is specified in Table A7.3. These values represent the highest concentration or quantity of a target variable that can be used as a reporting limit by the laboratory unless laboratory capabilities prohibit attaining an AWRL. AWRLs are program defined, and achieving them allows data to be evaluated against established freshwater criteria.

The limit of quantitation (LOQ) is the lowest concentration or quantity of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence. Analytical results shall be reported down to the laboratory's LOQ (i.e., the laboratory's LOQ for a given parameter is its reporting limit).

The following requirements must be met in order to report results under this QAPP:

- The laboratory's LOQ for each analyte must be equal to or less than the AWRL as a matter of routine practice.

- The laboratory must demonstrate its ability to achieve its LOQ for each analyte by analyzing an LOQ check standard (see Section B5) with each preparation batch of samples. Control limits for LOQ check standards are found in Table A7.3.

Laboratory Measurement Quality Control Requirements and Acceptability Criteria are provided in Section B5.

Precision

Precision is the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves. It is a measure of agreement among replicate measurements of the same property, under prescribed similar conditions, and is an indication of random error.

Laboratory precision is assessed by comparing replicate analyses of laboratory control samples in the sample matrix and sample/duplicate pairs. Precision results are compared against measurement performance specifications and used during evaluation of analytical performance. Program-defined measurement performance specifications for precision are defined in Table A7.3.

Representativeness

Initially, comparison grab samples will be taken from within the PVC tube, as near the sensors as possible, as water flows through the system and simultaneously with each sensor's sampling event. Due to the experimental nature of this project, sampling methods may change which may result in a limitation of representativeness.

Comparability

Project water quality data from laboratory measurements are based on *Standard Methods for the Examination of Water and Wastewater* (Standard Methods, 2016), latest online edition.

Completeness

The completeness of the TIAER Laboratory data is basically a relationship of how much of the data is available for use compared to total planned to be collected. Ideally, 100% of the data should be available. However, the possibility of unavailable data due to accidents, insufficient sample volume, broken or lost samples, etc. is to be expected. Therefore, it will be a general goal of the project(s) that 90% data completion is achieved.

A8 SPECIAL TRAINING/CERTIFICATION

SUNA V2 and Cycle-P

The TIAER site operator and other eligible TIAER staff members working on the project have received training from the manufacturer in operating and maintaining the Sea-Bird SUNA V2 sensor and Cycle-P analyzer.

TIAER Laboratory

Laboratory analysts have a combination of experience, education, and training to demonstrate knowledge of their function. To perform analyses for the TCEQ, laboratory analysts will have a demonstration of capability (DOC) on record for each test that the analyst performs. The initial DOC should be performed prior to analyzing samples and annually thereafter. For cases in which analysts have been analyzing samples prior to an official certification of capability being generated, a certification statement is made part of the training record to document the analyst's initial on the job training. The certifications statement is retained in the personnel file and will be available during audits. Annual DOCs are a part of analyst training thereafter. The TIAER laboratory is National Environmental Laboratory Accreditation Program (NELAP) accredited through TCEQ for parameters outlined for analysis in Table A7.3, as appropriate.

A9 DOCUMENTS AND RECORDS

Document/Record	Location	Retention	Form
Site Operator's Log	TIAER	5 years	Paper
QAPP, amendments, and appendices	TIAER	5 years	Paper/Electronic
QAPP distribution documentation	TIAER	5 years	Paper/Electronic
Field equipment maintenance logs	TIAER	5 years	Paper
Chain of custody records	TIAER	5 years	Paper/Electronic
Field SOPs	TIAER	5 years	Paper/Electronic
TIAER Laboratory sample reception logs	TIAER Lab	5 years	Paper/Electronic
TIAER Laboratory QA manuals	TIAER Lab	5 years	Paper/Electronic
TIAER Laboratory SOPs	TIAER Lab	5 years	Paper/Electronic
TIAER Lab Instrument raw data files	TIAER Lab	5 years	Paper/Electronic
TIAER Lab Instrument readings/printouts	TIAER Lab	5 years	Paper/Electronic
TIAER Laboratory data reports	TIAER Lab	5 years	Paper/Electronic
TIAER Laboratory equipment maintenance logs	TIAER Lab	5 years	Paper/Electronic
TIAER Laboratory calibration records	TIAER Lab	5 years	Paper/Electronic
TIAER Lab corrective action documentation	TIAER Lab	5 years	Paper/Electronic
Corrective Action Documentation	TIAER	5 years	Paper/Electronic
Progress report/final report/data	TIAER /TCEQ	3 years	Electronic

Backup/Disaster Recovery for Electronic Records

As an electronic data protection strategy, TIAER utilizes Vice-Versa software to mirror the Primary Aberdeen 4.5 TB file server (raid 5 fault tolerant) that will be mirrored to a secondary Aberdeen 3 TB file server (raid 5 fault tolerant). This provides instant fault recovery rollover capability in the event of hardware failure. TIAER also exercises complete backup of its Primary server to LTO-4 Quantum ValueLoader on a weekly basis, coupled with daily incremental backups. This provides a third level of fault tolerance in the event that both the primary and secondary servers are disabled. TIAER will maintain all cyclic backup tapes for 26 weeks. This will facilitate recovery of data lost due to human error. Backup tapes are stored in a secure area on the Tarleton University campus and are checked periodically to ensure viability. If necessary, disaster recovery can also be accomplished by manually re-entering the data.

B1 SAMPLING PROCESS DESIGN

Project Station

Station CAMS 725 is an existing station located on the North Bosque River watershed. The waterbody is perennial except during some dry summer months when it is pooled. See Figure A6.1 for station location. An existing trailer at the station will house the nutrient sensors and associated equipment.

Monitoring Station Design

The following describes the anticipated monitoring station design and is subject to change due to the experimental nature of this project.

The Cycle-P and SUNA V2 will be installed in the trailer at CAMS 725 for measuring dissolved orthophosphate phosphorus and nitrate-plus-nitrite nitrogen, respectively. Both instruments will monitor water quality in a flow-thru type system. Sampling for this system occurs by pumping stream water through an 8-inch diameter PVC tube (pipe) with an open top, which overflows into a larger tank and then back into the stream via a gravity-fed return line. Additionally, sample filtration occurs for the Cycle-P before the sensor via two parallel 10 micron filters built into the unit. Both instruments will be installed inside the 8-inch PVC tube and perform analyses at intervals to be determined. Initially the scheduled measurements will occur hourly (24 times per day), though the possibility of adjustment of this frequency is considered part of the experimental nature of this project. System operations and instrument sampling schedules will be controlled by a Sutron data logger which will also store the water quality data. See Figure A6.2 for sample delivery system and monitoring system design.

Comparison Grab Sampling

Periodically grab samples will be collected from the PVC tube for comparative OPO4-P and NO2-N+NO3-N analyses by the TIAER Laboratory. The number of comparative samples is limited by budget constraints on the project and the need to coordinate sample collection with other TIAER monitoring projects for purposes of inefficiency in laboratory analyses by reasonably sized sample batches. Statistical analyses will be performed to determine reliability of results obtained from the sensors as compared to laboratory results.

A minimum of 40 valid pairs of comparison grab samples and instrument readings is set for the project to allow adequate statistical testing of performance of both instruments against standard laboratory analytical methods. Comparative samples will be collected once every two weeks for a minimum period of one year to capture a range of environmental conditions. Biased sampling will also occur to allow sampling during high flow events to evaluate if any interference occurs under conditions of high total suspended solids. Changes to the above described comparative sampling protocol may be altered by email request from the TIAER PM and with email approval from the TCEQ PM without need to amend this QAPP.

B2 SAMPLING METHODS

SUNA V2 and Cycle-P

Monitoring Methods and Equipment

The two instruments are deployed in a climate-controlled trailer that contains a Sutron data logger, PC, and a Sierra Wireless LS300 IP modem. A submersible pump is deployed from the bridge into the North Bosque River, suspended by cables, to deliver water to and through the 8-inch PVC tube. Both instruments will be located inside the 8-inch PVC tube and will monitor nutrients as water flows through the system. Sample filtration occurs for the Cycle-P before the sensor via two parallel 10 micron filters built into the unit. Assessment of the reliability of this instrument configuration and water delivery is part of the project as well as the need to adjust and modify as needed to maximize performance of the instruments.

Nitrate-plus-nitrite nitrogen and orthophosphate phosphorus measurements are logged by the Sutron data logger on a schedule to be determined as part of the evaluation process. Initially the measurements will be made on an hourly basis (every 60 minutes). The data are also stored in each instrument and downloaded manually by TIAER staff. The data will be reviewed weekly, except during holidays or inclement weather events, by the TIAER site operator to determine if the analyzers are functioning properly.

Sampling/Measurement System Corrective Action

Situations associated with the SUNA V2 sensor and the Cycle-P analyzer that require corrective action will be handled as described in Section B2.2 of the CWQMN QAPP (TCEQ, 2015).

Consumable and replacement items (e.g. standards/reagents for Cycle-P analyzer and monitoring system supplies) for the instruments and monitoring system will be ordered directly from the manufacturer and/or obtained locally by TIAER staff.

TIAER Laboratory

For comparison grab sampling, TIAER staff will collect water quality grab samples from the 8-inch PVC tube, as near the sensor as possible, in coordination with the timing of sample analyses by the two sensors. These comparison grab samples will be filtered and/or preserved in the field, stored on ice, and transported to the TIAER laboratory for analyses of dissolved nitrate-plus-nitrite nitrogen and orthophosphate phosphorus. Grab samples will also be collected for analysis of total suspended solids (TSS), since turbidity is a potential confounding factor regarding reliability of results from the SUNA V2 and Cycle-P. The TIAER laboratory has NELAP accreditation for these three analyses.

Sample Containers

Sample containers are reusable plastic bottles, except for syringes, which are disposable containers. Syringes, which are used for field filtering, are acid washed upon receipt but only used once and then disposed. Reusable containers are thoroughly cleaned upon receipt before initial use and after each use, if reused. Reusable containers are cleaned by washing them in hot, soapy (non-phosphate) water.

Containers are then rinsed first in warm tap water, then with 1 M hot HCl,acid and finally rinsed at least three times in type II ASTM (American Society for Testing and Materials) water, i.e., water with conductivity of less than 1 microsiemen per centimeter. Containers are then placed on a rack to dry. The TIAER QAM-I-116 "Preparation of Labware" (TIAERb, 2015) contains specific steps used for cleaning sampling containers and equipment used in field operations and is available for review upon request.

Comparison Grab Sample Handling

TIAER staff will collect comparison grab samples that are as similar as feasible to samples analyzed by the sensors. The comparison grab sample will be obtained from the same 8-inch diameter PVC tube that provides samples for analysis to the sensors. Samples will be collected in polyethylene bottles that are 250 mL or smaller. The container types, preservation requirements, minimum sample volumes needed by the lab, and holding time requirements are specified in Table B2.1 for comparative grab samples, which will be analyzed for total NO_2-N+NO_3-N, field filtered PO_4-P through both a 0.45 micron and 10 micron filter, and total suspended solids. For PO_4-P the 10 micron filtered sample will mimic what occurs with the present Cycle-P sampling system and the 0.45 micron filtered sample is what is provided in the actual laboratory method specified by TCEQ for their ambient monitoring programs. The TSS measurement provides additional information that may prove useful regarding interference and sorption processes that may impact performance of the two instruments. Per the Standard Method 4500-NO3 F (Standard Methods), total NO_2-N+NO_3-N samples are neutralized for pH and filtered prior to insertion into the laboratory instrument.

All water quality grab samples will be handled according to procedures outlined in the most current *Surface Water Quality Monitoring* (SWQM) *Procedures Manual, Volume 1* (TCEQ, 2012). The samples will be iced in the field and submitted to the laboratory on ice the same day they are collected in the field, whenever possible. The sample bottle for PO_4-P analysis will be agitated thoroughly to ensure total mixing of sediments that may have settled, and then aliquots from the bottle will be filtered in the field, using a 0.45 micron membrane filter with a filtration flask and vacuum pump or in a 50 CC or larger syringe. An aliquot for NO_2-N+NO_3-N will be transferred to an acidified 50-mL plastic bottle, labeled as indicated above, capped, and shaken to disperse the acid in the sample. Samples too turbid for filtration in the field will be vacuum-filtered in the lab and preserved appropriately.

A minimum of 40 valid pairs of comparison grab samples and instrument readings is set for the project to allow adequate statistical testing of performance of both instruments against standard laboratory analytical methods. (See Section B1 for more details.)

Table B2.1 Sampling and Handling Procedures for Routine Stream Samples

Parameter	Matrix	Sample Type	Container	Field Preservation	Sample Volume	Holding Time
Nitrite + nitrate-Nitrogen, total	water	Grab	Pre-cleaned plastic	pH<2 with H_2SO_4, cool to >0-≤6ºC	50 mL	28 days
Total Suspended Solids	water	Grab	Pre-cleaned plastic	Cool to >0-≤6ºC	1000 mL*	7 days
Orthophosphate-P, dissolved	water	Grab	Pre-cleaned plastic	Filter within 15 minutes, cool to >0-≤6ºC	50 mL	48 hours

* - If a 1,000 mL sample volume cannot be obtained, the analyses will still be run, but the AWRL (Table A7.3) may have to be adjusted upward to compensate for reduced sample volume.

Sampling/Measurement System Corrective Action

Situations associated with TIAER sample handling and laboratory analysis will be addressed through TIAER's corrective action reporting system. The TIAER Project Manager, in consultation with the TCEQ Project Lead, will determine usability of data and types of corrective actions to be taken.

B3 SAMPLING HANDLING AND CUSTODY

SUNA V2 and Cycle-P

The SUNA V2 and Cycle-P instruments collect water samples via a sample line and submersible pump. The sample line and sample pot tube for the two instruments is flushed for several minutes with ambient water before the SUNA V2 sensor takes a reading and before a subsample is sent through a 10 micron filter and to the Cycle-P analyzer for a reading.

TIAER Laboratory

Comparison grab sample handling, transportation, and storage will follow guidelines in the most recent version of *Surface Water Quality Monitoring Procedures, Volume 1* (TCEQ, 2012), unless otherwise noted.

Sample Labeling

Water quality samples are labeled on the container with an indelible marker. Label information from the field crew includes:

1. Station identification
2. Time of sampling
3. Date of sampling
4. Preservation/bottle code

These unique identifiers on the sample container can be matched with data on the Chain of Custody (COC) forms submitted to the laboratory. Laboratory personnel then add information on container type ID designation, test group code, and sample number when logging in the samples, so the parameters to be analyzed from each container are clearly indicated.

The field staff member documents on a field data sheet the station, date, time, location, and sample type and pertinent comments. These identifying data are copied in ink onto a hardcopy COC or typed onto a computer-generated COC. A unique sample identification number is assigned to water samples at the TIAER office and written in indelible ink on the sample container and on the COC. The sample identification number, time, date and station location serve to match the sample with data on the COC.

Sample Tracking

Proper sample handling and custody procedures ensure the custody and integrity of samples beginning at the time of sampling and continuing through transport, sample receipt, preparation, and analysis.

A sample is in custody if it is in actual physical possession or in a secured area restricted to authorized personnel. The COC form is used to document sample handling during transfer from the field to the laboratory. The following information concerning the sample is recorded on the TIAER COC form.

1. Date and time of collection
2. Site identification
3. Sample matrix
4. Number of containers and container type ID designation
5. Preservative used or if the sample was filtered, indicated by preservative/container code
6. Analyses required, indicated by test group code
7. Name of collector
8. Custody transfer signatures and dates and time of transfer
9. Name of laboratory admitting the sample

Sample Tracking Procedure Deficiencies and Corrective Action

All deficiencies associated with chain-of-custody procedures described in this project plan are immediately reported to the TIAER Project Manager. These include items such as delays in transfer resulting in holding time violations; violations of sample preservation requirements; incomplete documentation, including signatures; possible tampering of samples; and broken or spilled samples. The TIAER Project Manager, in consultation with the TIAER Project QAO, will determine if the procedural violation may have compromised the validity of the resulting data. Any failures that have reasonable potential to compromise data validity will invalidate data and, if possible, the sampling will be repeated.

The definition of and process for handling deficiencies, non-conformances, and corrective action are defined in Section C1.

B4 ANALYTICAL METHODS

SUNA V2 and Cycle-P

Project measurement equipment and analytical methods are listed in Tables B4.1

Table B4.1 SUNA V2 and Cycle-P Analytical Methods

Parameter	LEADS Parameter Code	Units	Measurement Equipment	Method
Nitrate+Nitrite Nitrogen	TBD	mg NO2+3 as N/L	SUNA V2	Optical (UV absorption)
Orthophosphate Phosphorus	TBD	mg PO4 as P/L	Cycle-P	Optical (colorimetric: EPA 365.5)*

* Method is based on EPA 365.5 with the exception of the use of a 10 micron filter instead of a 0.45 micron filter.

TIAER Laboratory

The analytical methods are listed in Table A7.3 of Section A7. The TIAER Laboratory is compliant with The NELAC Institute (TNI) Standards. The TIAER is NELAP accredited via TCEQ for the parameters to be evaluated under this QAPP. Copies of laboratory SOPs are retained by TIAER and are available for review by the TCEQ. Laboratory SOPs are consistent with EPA requirements as specified in the method.

B5 QUALITY CONTROL

SUNA V2 and Cycle-P

Quality control for the SUNA V2 and Cycle-P will be developed for and included in the SOPs being developed for each instrument under this project. Data records for analyses completed by Sea-Bird Coastal sensors are not validated by TCEQ under their normal protocol due to the experimental nature of this project. Initial quality control consists of annual sensor calibrations and periodic sensor and PVC tube cleaning. For the SUNA V2, inclusion of the integrated wiper assembly and periodic reference spectra updates will address sensor fouling.

TIAER Laboratory

Water quality measurement methods used by the TIAER Laboratory are based on *Standard Methods for the Examination of Water and Wastewater* (Standard Methods, 2016), online, and are described in TIAER's laboratory SOPs for the NELAP-certified analyses. Section A7 summarizes procedures and quality objectives for the project.

Laboratory Measurement Quality Control Requirements and Acceptability Criteria

Refer to TIAER SOP "QAM-Q-101, Laboratory Quality Control" (TIAER, 2015d).

Quality Control or Acceptability Requirement Deficiencies and Corrective Actions

Refer to TIAER SOPs "QAM-Q-100, Quality Assurance Manual" (TIAERa 2015c) and "QAM-Q-105, Corrective Actions" (TIAER, 2015g).

Statistical Analyses on Comparative Samples

An important objective of this project is to compare results from the Cycle-P and SUNA V2 to standard analytical laboratory methods. Statistical matched-pair tests will be used to make these comparisons based on the study design which incorporates taking a water sample for laboratory analysis in close temporal proximity to the readings by the Cycle-P and SUNA V2, and from the same water inside the 8-inch PVC containing the two instruments. If the difference between the pairs of data are normally distributed, then the parametric paired t-test will be employed. If normality is not indicated using the Shapiro-Wilk test, then the nonparametric statistics of the Sign Test and Signed-Rank Test will be applied. These matched-pair test will be used to determine if one group of results contains larger values than the other group. Simple linear regression analysis of the pairs with correlation analysis will also be used to investigate the relationship of the paired data. Scatterplots and regression analyses will be used to investigate the occurrence of any interference from TSS on the readings obtained from both instruments. Other statistical analyses may be employed as driven by the results from the immediately above analyses.

B6 INSTRUMENT/EQUIPMENT TESTING, INSPECTION AND MAINTENANCE

SUNA V2 and Cycle-P

As part of the project, TIAER will develop the SOP for each instrument, including cleaning and maintenance procedures. The newly deployed instrument are under warranty for one year after installation Technical support for troubleshooting is provided via phone or email by Sea-Bird Coastal.

TIAER Laboratory

All laboratory tools, gauges, instrument, and equipment testing and maintenance requirements are described in laboratory SOP "QAM-Q-100, Quality Assurance Manual" (TIAER, 2015c). Testing and maintenance records are available for inspection by TCEQ. Instruments requiring daily or in-use testing may include, but are not limited to, water baths, ovens, autoclaves, incubators, refrigerators, and laboratory pure water. Critical spare parts for essential equipment are maintained to prevent downtime. Maintenance records are available for inspection by TCEQ.

B7 INSTRUMENT CALIBRATION AND FREQUENCY

SUNA V2 and Cycle-P

For this project, both sensors will be deployed for continuous monitoring purposes over a deployment period of several months. Both sensors will be calibrated by the manufacturer before and after each deployment, to occur annually, but may be more frequent depending on sensor performance. For information concerning Sea-Bird Coastal sensor specific calibrations, see manufacturer's documentation.

TIAER Laboratory

Detailed laboratory calibrations are contained within the TIAER Laboratory SOPs. Individual SOPs identify all tools, gauges, instruments, and other sampling, measuring, and test equipment used for data collection activities affecting quality that must be controlled and, at specified periods, calibrated to maintain bias within specified limits. Calibration records are maintained and are available for inspection by the TCEQ. Instruments requiring periodic calibration include, but are not limited to, thermometers, pH meters, balances, incubators, and analytical instruments. Calibration records are available to the TCEQ for review.

B8 INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

As described in Section B8 of the CWQMN QAPP (TCEQ, 2015). TIAER will purchase supplies as necessary per project requirements. TCEQ or TIAER will purchase reagent refills for the Cycle-P as stipulated contractually.

B9 NON-DIRECT MEASUREMENTS

The sole non-direct measurement used on this project will be real-time, instantaneous streamflow from the U.S. Geological Survey (USGS) North Bosque River streamflow gage 08094800 at Hico, Texas. The streamflow from this gage will be used as an estimate of the flow at CAMS 725. When comparative samples are collected for analysis by the TIAER Laboratory, the instantaneous streamflow at gage 08094800 will be obtained for the date and time of the sample collection. The USGS is considered a reliable source of data and their data are readily available on-line at:

http://waterdata.usgs.gov/nwis/uv?08094800

B10 DATA MANAGEMENT

SUNA V2 and Cycle-P

Project data are stored onboard each instrument and collected by a Sutron data logger housed on site.

Project data collected for this project will not be validated or loaded into SWQMIS.

TIAER Laboratory

Data Path

Water quality samples are collected and transferred from the field to the laboratory for analyses as described in Section B3 using a COC form following procedures in TIAER "QAM-Q-110, Sample Receipt and Login" (TIAER, 2015h). Refer to this procedure, "QAM-Q-100, Quality Assurance Manual" (TIAER, 2015c), and "QAM-Q-104, Laboratory Data Entry and Review" (TIAER, 2015f).

Record-keeping and Data Storage

TIAER record-keeping and document control procedures are contained in the TIAER QAM and this QAPP. Original field and laboratory data sheets are stored in the TIAER offices, laboratory, and storage facilities in accordance with the record-retention schedule in Section A9. Refer to TIAER SOP "QAM-A-102, Laboratory Document and Data Control" (TIAER, 2015a).

Data Verification/Validation

The control mechanisms for detecting and correcting errors and for preventing loss of data during data reduction, data reporting, and data entry are contained in Sections D1, D2, and D3.

Data Handling

Refer to TIAER SOP "QAM-Q-104, Data Entry and Review" (TIAER, 2015f).

Hardware and Software Requirements

Hardware configurations are sufficient to run Microsoft Access and SAS software in a networked environment. TIAER information resources staff is responsible for assuring that hardware configurations meet the requirements for running current and future data management/database software as well as providing technical support. Software development of the ESDMS and SAS applications are based on user requests and are tested for reliability prior to implementation.

C1 ASSESSMENTS AND RESPONSE ACTIONS

Laboratory Assessments

The TIAER laboratory is NELAP accredited for the methods, matrices, and parameters that are to be analyzed as part of this project.

In accordance with Title 30 of the Texas Administrative Code (TAC), §25.20 (TAC, 2016), the TIAER laboratory must successfully analyze at least two proficiency test samples, if available, each year for each field of accreditation. Specific requirements for proficiency testing are detailed in Volume 1, Module 1, of the 2009 TNI Standard (TNI, 2009).

30 TAC §25.18 (TAC, 2016) requires that the TIAER laboratory be assessed every two years by TCEQ as the NELAP accrediting body. Responses to findings as a result of assessments are to be submitted to TCEQ within 30 calendar days of receipt of the audit report.

Project Assessments

The TIAER Project Manager performs continuous oversight of the project status and records to ensure that the project objectives are being fulfilled and that TCEQ requirements are being met. The TIAER site operator periodically monitors the station's measurement data for deficiencies. If problems are identified, the site operator shall initiate corrective action, which may require a site visit to further investigate the root cause.

When problems are identified that cannot be resolved by the site operator, the site operator notifies the TCEQ Project Manager. The TCEQ Project Manager is responsible for coordination with appropriate personnel to resolve the problems. The TCEQ Project Manager is also responsible for documenting and verifying completion of all corrective actions.

Station readiness reviews may be conducted at the beginning of a new project to ensure a project is functioning correctly. Readiness reviews may also be conducted after a major change to an existing project.

No minimum number of assessments are specified for this project

Corrective Action

As described in Section C1 of the CWQMN QAPP.

Any TIAER staff member who discovers a problem will initiate corrective action appropriate to the situation. Corrective action is accomplished at the lowest level and shall be documented in the TIAER site operator log for the project. The TIAER Project Manager will be notified of any proposed corrective action that can affect data quality and/or project protocols. Refer to TIAER procedure "QAM-Q-105, Corrective Actions" (TIAER, 2015g).

C2 REPORTS TO MANAGEMENT

Reports to TCEQ Project Management

Quarterly Progress Report - Summarizes the TIAER's activities for the project; reports problems, delays, and corrective actions; and outlines the status of task deliverables.

Summary Annual Report - Includes all operational findings developed for the project.

Working Draft Standard Operating Procedures – initial development of standard operating procedures in separate documents for the SUNA V2 and Cycle-P.

Reports to TIAER Project Management

Corrective Action Reports (CARs) are the primary mechanism for communicating significant QA issues to management. Also on approximately a weekly basis, the TIAER PM routinely interacts with the project site operator and lab manager in coordinating sampling events and any issues that arise with sensor data production, sample collection or analysis. TIAER project staff are also queried about progress on project deliverables and any problems or issues concerning project activities by the TIAER PM in preparing monthly progress reports.

D1 DATA REVIEW, VERIFICATION, AND VALIDATION

Project data collected from the Sea-Bird Coastal instruments will not be validated, because of the experimental nature of the project.

All data obtained from TIAER laboratory measurements will be reviewed and verified for conformance to project requirements, and then validated against the data quality objectives listed in Section A7. Only those data supported by appropriate quality control data that meet the measurement performance specification defined for this project will be considered acceptable and used in comparisons to data collected from the Sea-Bird Coastal sensors.

D2 VERIFICATION AND VALIDATION METHODS

Project data from the Sea-Bird Coastal sensors are not verified independently.

Verification, validation and integrity review of TIAER laboratory data will be performed using self-assessments and peer review, as appropriate to the project task, followed by technical review by the manager of the task. The data to be verified are evaluated against project performance specifications and are checked for errors, especially errors in transcription, calculations, and data input. If a question arises or an error is identified, the manager of the task responsible for generating the data is contacted to resolve the issue. Issues that can be corrected are corrected and documented electronically or by initialing and dating the associated paperwork. If an issue cannot be corrected, the task manager consults with higher level project management to establish the appropriate course of action, or the data associated with the issue are rejected.

D3 RECONCILIATION WITH USER REQUIREMENTS

As described in Section D3 of the CWQMN QAPP (TCEQ, 2015) and further qualified by the experimental focus of this project.

Appendix A

FY 2016 & 2017 Project Scope of Work

Project: Evaluation of Continuous Nutrient Monitoring Sensors and Analyzers

TCEQ will contract with the Texas Institute for Applied Environmental Research (the "Performing Party") for evaluation and documentation of nutrient sensors and analyzers at one continuous water quality monitoring station in the North Bosque River watershed at State Highway 6 for the term of the Contract.

In anticipation of future requests for continuous nutrient monitoring, TCEQ is investigating two nutrient analyzers: 1) SUNA v2 nitrate analyzer; and 2) a Cycle-P phosphate analyzer. TCEQ is contracting with the Performing Party to operate and maintain both instruments in a flow-thru environment, to evaluate the instruments and develop Working Draft and Final Standard Operating Procedures for the instruments.

Specifically, the Performing Party will:

- Operate and maintain the SUNA v2 and Cycle-P at CAMS 725 in a flow-thru sampling system;
- Test the results of the instruments against laboratory results for field-split water samples;
- Develop and maintain Working Draft and Final Standard Operating Procedures for the SUNA v2 nitrate sensor; and,
- Develop and maintain Working Draft and Final Standard Operating Procedure for the Cycle-P phosphate analyzer.

OBJECTIVE 1: PROJECT ADMINISTRATION

Goal: To effectively coordinate and monitor all technical and financial activities performed under this Contract, prepare regular progress reports, and manage project files and data.

Task 1.1 **Project Oversight** – The Performing Party will provide technical and fiscal oversight of the Performing Party project staff to ensure Tasks and deliverables are acceptable, completed as scheduled, and within budget. With the TCEQ Project Manager's authorization, the Performing Party may secure the services of subcontractor(s) as necessary for technical support, repairs and training. Project oversight status will be provided to TCEQ with the Monthly Progress Reports (MPRs).

Task 1.2 **MPRs** – The Performing Party will submit MPRs to TCEQ by the 15th of the month during the term of the Contract. MPRs will contain a level of detail sufficient to document the activities that occurred under each Task during the previous month and will contain a comprehensive tracking of deliverable status under each Task.

Task 1.3 **FSRs** – The Performing Party will submit FSRs to TCEQ 30 days after the close of each state fiscal quarter.

For the last reporting period of the Contract (June, July, and August), reimbursement requests are required on a monthly basis. The Performing Party will submit the monthly reimbursement request documents within fifteen (15) days after the close of each month with the exception of the final billing which is due within 45 days after the close of the Contract.

Task 1.4 **Contract Communication** – The Performing Party will initiate, participate in, and document a post-award orientation meeting with TCEQ within 30 days of Contract execution. The Performing Party will maintain regular telephone and/or email communication with the TCEQ Project Manager regarding the status and progress of the project and any matters that require attention between MPRs. Matters that must be communicated to the TCEQ Project Manager in the interim between MPRs may include the following:

- Requests for prior approval of activities or expenditures for which the Contract requires advance approval or that are not specifically included in the Scope of Work; and
- Information regarding events or circumstances that may require changes to the Budget, Scope of Work, or Schedule of Deliverables. Such information must be reported within two working days of discovering these events or circumstances.

Task 1.5 **Contractor Evaluation** – The Performing Party will participate in an annual Contractor Evaluation at the end of each state fiscal year.

Measures of Success:
- Adherence to TCEQ's administrative requirements; timely completion and submittal of MPRs and deliverables.

Deliverables:
- MPRs;
- FSRs;
- Minutes of Post-Award Orientation Meeting; and,
- Participation in contractor evaluations.

OBJECTIVE 2: EVALUATE NUTRIENT SENSORS

Goal: To evaluate nutrient sensors and develop Working Draft SOPs for the sensors.

Task 2.1: **Operation and Maintenance of one Continuous Water Quality Monitoring Network (CWQMN) Station on the North Bosque River -** The Performing Party will operate and maintain CWQMN station CAMS 725 on the North Bosque River at State Highway 6 (Table 3.1 below) for the term of the Contract or until available funding is expended, whichever occurs first. The Performing Party will operate and maintain the analyzers at CAMS 725 in a flow-thru sampling system and compare results from the instruments against field-split samples analyzed in the laboratory. The Performing Party will develop and maintain Working Draft Standard Operating procedures for the SUNA v2 nitrate sensor and the Cycle-P phosphate analyzer and submit monthly progress reports and a summary project report.

Table 2.1 – Performing Party Operated CWQMN Stations, Parameters and Objectives

CAMS	Station Description	Parameters Monitored	Objectives
725	North Bosque River at State Highway 6	SRP, NO3	To demonstrate and document the performance of the SUNA v2 and the Cycle-P.

Legend: ~SRP=Soluble Reactive Phosphorus; and NO3=Nitrate

Measures of Success:
- Testing of SUNA v2 and Cycle-P against laboratory results; and,
- Deployment of SUNA v2 and Cycle-P at CAMS 725

Deliverables:

- Monthly status report including data completeness and issues identified and resolution/status of the issues in WORD or EXCEL format;
- Working Draft Standard Operating Procedure for SUNA v2 in MS-WORD consistent with TCEQ CWQMN SOP format by 8/31/2016;
- Final Standard Operating Procedure for SUNA v2 in MS-WORD consistent with TCEQ CWQMN SOP format by 8/31/2017;
- Working Draft Standard Operating Procedure for Cycle-P in MS-WORD consistent with TCEQ CWQMN SOP format by 8/31/2016;
- Final Standard Operating Procedure for Cycle-P in MS-WORD consistent with TCEQ CWQMN SOP format by 8/31/2017; and,
- Project Summary Report.

OBJECTIVE 3: QAPP DEVELOPMENT

Goal: To conduct data collection activities in accordance with an integrated system of quality management activities involving planning, assessment, implementation, training, and quality.

Task 3.1 **QAPP for Monitoring** – The Performing Party will review and comment on TCEQ CWQMN QAPP revisions annually and will conduct all water quality monitoring for the CWQMN station on the North Bosque River at State Highway 6 under the current revision of the TCEQ CWQMN QAPP.

Task 3.2 **Records Access and Audit –** The Performing Party will be available for technical audits by TCEQ. The Performing Party will maintain books, records, documents, and other evidence reasonably pertinent to performance of the work and requirements of the Contract documents, including the Contract and Amendments during the term of the Contract and for a minimum of three (3) years thereafter. The Performing Party will receive a written Audit Report describing all findings. The Performing Party will respond within thirty (30) days to any findings in the Audit Report.

Measures of Success:

- The Performing Party's review and comment on the TCEQ CWQMN QAPP revisions and conformance to TCEQ CWQMN QAPP; and
- The Performing Party's response to audit findings within thirty (30) days of receiving the Audit Report.

Deliverables:

- The Performing Party's comments on the TCEQ CWQMN QAPP revisions annually in December.

Appendix B
List of References

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