Assessment of Non Point Source Pollution from Cropland in the Oso Bay Watershed
(Project 07-07)

Quality Assurance Project Plan
Revision No. 0
25 January 2008

Prepared by
Texas AgriLife Research and Extension Center at Corpus Christi
Texas A&M System
10345 State HWY 44
Corpus Christi, Texas   78406-1412

Funding source:

Clean Water Act Section 319(h)
Nonpoint Source Pollution Control Program Project
in cooperation with
Texas State Soil and Water Conservation Board
and
U.S. Environmental Protection Agency

Effective Period: September 2007 to August 2009

Questions concerning this quality assurance project plan should be directed to:

Dr. Carlos J. Fernandez, Associate Professor
Texas AgriLife Research and Extension Center at Corpus Christi
10345 State HWY 44
Corpus Christi, TX 78406-1412
(361) 265-9201

cj-fernandez@tamu.edu

A1 Approval Page

Assessment of NPS Pollution from Cropland in the Oso Bay Watershed

United States Environmental Protection Agency (USEPA), Region 6

Name: Donna Miller
Title: Chief State/Tribal Programs Section

Signature: Donna R. Miller Date: 6/19/08

Name: Ellen Caldwell
Title: Project Officer Assistance Programs Branch

Signature: Ellen Caldwell Date: 6-12-08

Texas State Soil and Water Conservation Board (TSSWCB)

Name: Mitch Conine
Title: Project Manager

Signature: Mitch Conine Date: 27 May 2008

Name: Donna Long
Title: Quality Assurance Officer

Signature: Donna K. Long Date: 5/27/08

Texas AgriLife Research

Name: Dr. Carlos J. Fernandez
Title: Associate Professor; Project Manager/QA Manager

Signature: C Fernandez Date: 22 May 2008

United States Geological Survey – San Antonio Subdistrict Office (USGS-SA)

Name: George Ozuna
Title: USGS Chief, San Antonio Water Science Center

Signature:________________ Date: 4.30.08

Name: Darwin Ockerman
Title: USGS Project Chief, San Antonio Water Science Center

Signature:________________ Date: 4/30/08

Name: Stephanie Marr
Title: USGS San Antonio Water Science Center Project Quality Assurance Officer

Signature: Stephanie L. Marr Date: 04-30-2008

United States Geological Survey – National Water Quality Laboratory (USGS-NWQL)

For Name: Gregory Mohrman
Title: Chief, USGS, NWQL

Signature:________________ Date: 5/14/08

United States Geological Survey – Iowa Sediment Laboratory

Name: Julie Nason
Title: Acting Chief, USGS Iowa Water Science Center Sediment Laboratory

Signature: Julie Nason Date: 5/16/08

Texas A&M University – Corpus Christi – Environmental Microbiology Laboratory

Name: Joanna Mott
Title: Professor of Biology

Signature: Joanna Mott Date: 05/22/08

Section A2 Table of Contents

Section: Title **Page**

A3 Distribution List

United States Environmental Protection Agency, Region 6
6WQ-AT
1445 Ross Avenue, Suite 1200
Dallas, TX 75202-2733

Name: Ellen Caldwell
Title: Project Officer

Texas State Soil and Water Conservation Board
P.O. Box 658
Temple, TX 76503

Name: Mitch Conine
Title: Project Manager

Name: Donna Long
Title: Quality Assurance Officer

Texas AgriLife Research and Extension Center at Corpus Christi
10345 State HWY 44
Corpus Christi, TX 78406-1412

Name: Carlos J. Fernandez
Title: Project Leader/QA Manager

U.S. Geological Survey, San Antonio Subdistrict
5563 De Zavala Rd., Suite 290
San Antonio, TX 78249

Name: George Ozuna
Title: USGS Chief, San Antonio Office

Name: Darwin Ockerman
Title: USGS Project Chief

Name: Stephanie Marr
Title: USGS Project Quality Assurance Officer

U.S. Geological Survey, National Water Quality Laboratory
P.O. Box 25046, MS 407, Bldg. 95
Denver Federal Center
Denver, CO 80225-0046

Name: Gregory Mohrman
Title: Chief, USGS, NWQL

U.S. Geological Survey, Water Science Center, Sediment Laboratory
P.O. Box 1230
Iowa City, IA 52244

Name: Julie Nason
Title: Acting Chief

Texas A&M University – Corpus Christi – Environmental Microbiology Labroatory
Name: Joanna Mott, Ph.D.
Title: Laboratory Manager

The Texas Agrilife Research and Extension Center at Corpus Christi will provide copies of this project plan and any amendments or appendices of this plan to each person on this list. The Texas Agrilife Research and Extension Center at Corpus Christi will document distribution of the plan and any amendments and appendices, maintain this documentation as part of the project's quality assurance records, and will be available for review.

List of Acronyms

BMP	best management practices
BOD	biochemical oxygen demand
CAR	corrective action report
CBBEP	Coastal Bend Bays and Estuaries Program
COC	chain of custody
CWA	Clean Water Act
DQO	data quality objectives
EMC	event mean concentration
EPA	Environmental Protection Agency
GM	general maintenance
GOES	Geostationary Operational Environmental Satellite
ID	identification
LCS	laboratory control standards
LCSD	laboratory control standard duplicate
MDL	method detection limit
MS	matrix spike
NIST	National Institute for Standards and Technology
NO_2+NO_3-N	nitrite+nitrate-nitrogen
NPDES	National Pollutant Discharge Elimination System
NPS	nonpoint source
NRCS	Natural Resources Conservation Service
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
QA	quality assurance
QAM	quality assurance manual
QAO	quality assurance officer
QAPP	quality assurance project plan
QC	quality control
QMP	quality management plan
P	phosphorus
PD	percent deviation
pH	potential hydrogen
PM	project manager
PO_4-P	orthophosphate phosphorus
Research	Texas AgriLife Research
RL	reporting limit
RPD	relative percent difference
SCN	sample control number
SOP	standard operating procedures
SWCD	Soil and Water Conservation District
SWQM	surface water quality monitoring
TAMU	Texas A&M University
TCEQ	Texas Commission on Environmental Quality
TKN	total kjeldahl nitrogen
TMDL	total maximum daily load
TP	total phosphorus
TSS	total suspended solids
TS	total solids

TSSWCB	Texas State Soil and Water Conservation Board
USDA-NRCS	United States Department of Agriculture Natural Resources Conservation Commission
USGS	United States Geological Survey
USGS-NWQL	United States Geological Survey – National Water Quality Laboratory
USGS-QAPP	United States Geological Survey – Quality Assurance Project Plan
USGS-QMS	United States Geological Survey – Quality Management System
USEPA	United States Environmental Protection Agency
WQMP	Water Quality Management Plan

A4 Project/Task Organization

The following is a list of individuals and organizations participating in the project with their specific roles and responsibilities:

USEPA – United States Environmental Protection Agency (USEPA), Region 6, Dallas.
Provides project overview at the Federal level.

Ellen Caldwell, Project Officer Assistance
Programs Branch
Responsible for overall performance and direction of the project at the Federal level. Ensures that the project assists in achieving the goals of the federal Clean Water Act (CWA). Reviews and approves the quality assurance project plan (QAPP), project progress, and deliverables.

TSSWCB – Texas State Soil and Water Conservation Board (TSSWCB), Temple, Texas.
Provides project overview at the State level.

Mitch Conine, Project Manager
Responsible for ensuring that the project delivers data of known quality, quantity, and type on schedule to achieve project objectives. Tracks and reviews deliverables to ensure that tasks in the work plan are completed as specified.

Donna Long, Quality Assurance Officer
Reviews and approves QAPP and any amendments or revisions and ensures distribution of approved/revised QAPPs to TSSWCB and USEPA participants. Responsible for verifying that the QAPP is followed by project participants. Determines that the project meets the requirements for planning, quality assessment (QA), quality control (QC), and reporting under the CWA Section 319 program. Monitors implementation of corrective actions. Coordinates or conducts audits of field and laboratory systems and procedures.

Texas AgriLife Research. Texas AgriLife Research (hereinafter referred as Research) is an agency of the Texas A&M System. Project Manager. Provides the primary point of contact between the Texas State Soil and Water Conservation Board (TSSWCB) and the project contractors. Tracks and reviews deliverables to ensure that tasks in the work plan are completed as specified. Responsible for coordination, review, and delivery of quarterly reports and the final project report.

Carlos J. Fernandez, Research; Associate Professor, Project Manager/QA Manager
Primary contact with property owners; responsible for ensuring that tasks and other requirements in the contract are executed on time and as defined by the grant work plan; assessing the quality of work by participants; submitting accurate and timely deliverables and costs to the TSSWCB Project Leader, and coordinating attendance at conference calls, meetings, and related project activities. Responsible for determining that the Quality Assurance Project Plan (QAPP) meets the requirements for planning, quality control, quality assessment, and reporting for activities conducted by Research. Responsible for maintaining records of QAPP distribution, including appendices and amendments. Coordinates the research and review of technical QA material and data related to water quality monitoring system design and analytical techniques. Responsible for installation, maintenance, troubleshooting, and repair of gaging and sampling stations and instrumentation, responsible for sample collection, processing, and shipment of samples to NWQL; assists USGS in delineating boundaries of watersheds gaged by streamgage stations; oversees site maintenance (mowing); coordinates and supervises field sampling activities. Responsible for ensuring that field personnel have adequate training and a thorough knowledge of standard operating procedures (SOPs) specific to the analysis or task performed and/or

supervised. Responsible for ensuring that tasks and other requirements in the contract are executed on time and in accordance with the QA/QC requirements in the system as defined by the contract work plan and in the QAPP. Responsible for verifying that the data produced are of known and acceptable quality. Responsible for ensuring adequate training and supervision of all activities involved in generating analytical data for this project. Responsible for the facilitation of audits and the implementation, documentation, verification, and reporting of corrective actions. Responsible for submitting accurate and timely data analyses and other materials for progress and final reports to Research.

USGS – U.S. Geological Survey (USGS), San Antonio, Texas, Water Science Center. Subcontractor to Research for conduct of the project. Works jointly with Research in carrying out objectives of the study.

George Ozuna, Chief, USGS San Antonio, Water Science Center. Responsible for supervision of USGS hydrologic investigations in South Texas.

Darwin Ockerman, Project Chief, USGS, San Antonio Water Science Center. Responsible for USGS overall project operations in South Texas. Responsible for delineating boundaries of watershed gaged by streamgage stations; assists Research with installation, maintenance, troubleshooting, and repair of gages and sampling stations and instrumentation; responsible for streamgaging, provides direction and assists Research with sample collection, processing and shipment; responsible for maintenance of streamflow and precipitation data base; publishes a USGS report summarizing the results of the study.

Stephanie Marr, Project Quality Assurance Officer, USGS, San Antonio Water Science Center.
Responsible for maintenance of water-quality data base for NWQL analyses; responsible for maintenance of sediment data base for USGS sediment laboratory analyses; responsible for monitoring water-quality sampling procedures and quality-assurance practices and procedures.

USGS, NWQL - U.S. Geological Survey, National Water Quality Lab (USGS, NWQL), Denver, Colorado. Provides laboratory analysis of water quality samples. Responsible for data analysis and reporting tasks for the project.

Gregory Mohrman, Chief, NWQL. Responsible for supervising NWQL chemistry laboratory personnel involved in generating analytical data for this project. Responsible for ensuring that laboratory personnel involved in generating analytical data have adequate training and knowledge of all standard operating procedures (SOPs) specific to the analysis or task performed and/or supervised. Responsible for oversight of all laboratory operations and ensuring that all quality assurance-quality control requirements are met. The NWQL management structure provides clear lines of authority and responsibility to help ensure timely, informed decision making. The laboratory is comprised of Sections, each with its own manager and subordinate supervisors as required. All Section chiefs report to the NWQL chief and are accountable for specific mission and functional elements specified in sections 2.1 – 2.3 of the NWQL Quality Management System (QMS) (Appendix F). The NWQL will coordinate with the USGS Project Chief (Darwin Ockerman) and USGS Project Quality Assurance Officer (Stephanie Marr) concerning quality assurance issues and circumstances that might adversely affect the quality of data.

USGS - U.S. Geological Survey, Sediment Laboratory, Iowa City, Iowa,
Provides laboratory analysis of water quality samples. Responsible for data analysis and reporting tasks for the project.

Julie Nason, Sediment Laboratory Acting Chief. Responsible for supervising sediment laboratory personnel involved in generating analytical data for this project. Responsible for ensuring that laboratory personnel involved in generating analytical data have adequate training and knowledge of all standard operating procedures (SOPs) specific to the analysis or task performed and/or supervised. Responsible for oversight of all laboratory operations and ensuring that all quality assurance-quality control requirements are met. Responsible for documentation related to laboratory analyses. Enforces corrective action, as required. The Sediment Laboratory will coordinate with the USGS Project Chief

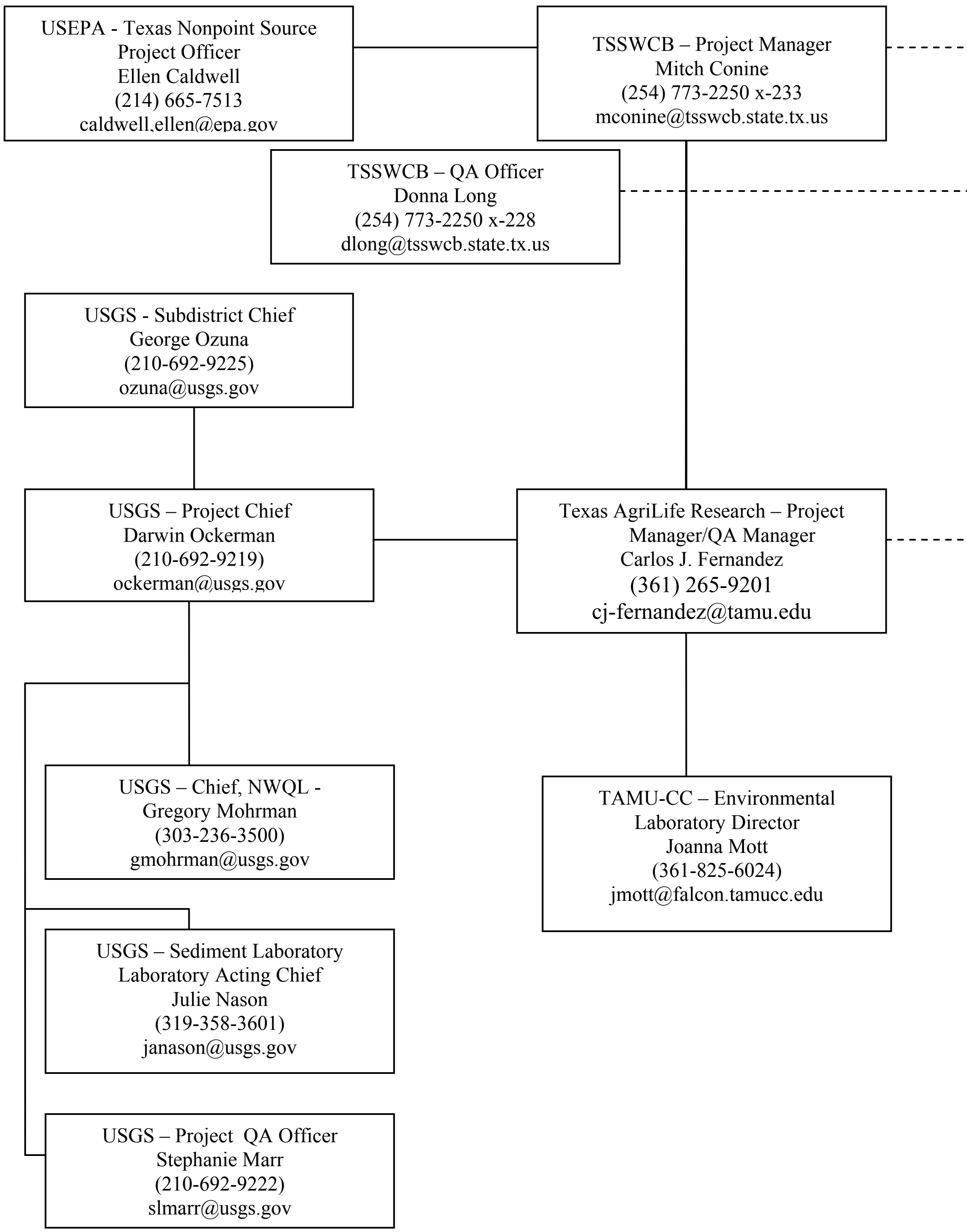
(Darwin Ockerman) and USGS Project Quality Assurance Officer (Stephanie Marr) concerning quality assurance issues and circumstances that might adversely affect the quality of data.

TAMU – Texas A&M University – Corpus Christi – Environmental Microbiology Laboratory

Joanna Mott, Associate Professor; Laboratory Manager
Responsible for supervision of laboratory personnel involved in generating bacteria data for the project. Responsible for ensuring that laboratory personnel involved in generating analytical data have adequate training and a thorough knowledge of the QAPP and all SOPs specific to the analyses or task performed and/or supervised. Responsible for oversight of all laboratory operations ensuring that all QA/QC requirements are met, documentation related to the analysis is complete and adequately maintained, and that results are reported accurately. Responsible for ensuring that corrective actions are implemented, documented, reported, and verified.

Figure A4 Project Organization Chart

Dashed lines indicate communication only



A5 Problem Definition

The TSSWCB and the Texas Commission on Environmental Quality (TCEQ) implement statewide approach for watershed management in Texas to improve the efficiency, effectiveness, and continuity of water quality management programs. The approach, which is summarized in *Texas Nonpoint Source Management Program* (TCEQ/TSSWCB, 2005), establishes the state's process for managing water quality. It focuses on assessing watershed conditions for all waters of the state and implementing solutions where improvement is necessary. The primary goal of the approach is to ensure that management efforts protect and restore water quality from point and nonpoint source pollution through assessment, implementation, and education. This, in turn provides a safe, clean, affordable water supply and healthy aquatic ecosystems for Texas. The TSSWCB has statewide responsibility for the agricultural and silviculture components of the management program.

The Total Maximum Daily Load (TMDL) Program, a component of the approach, addresses impaired streams, lakes, and estuaries (water bodies). The primary objective of the TMDL Program is to restore and maintain the beneficial uses of impaired water bodies. The Federal Clean Water Act §303(d) list identifies "impaired" water bodies not meeting applicable water quality standards for their designated uses and requiring development of Total Maximum Daily Loads (TMDLs) for contaminants of concern. In general, a TMDL is the total amount of a pollutant that a water body can assimilate and still meet state water quality standards. The term also refers to the assessment (and resulting report) necessary to establish an acceptable pollutant load for an impaired water body and to allocate the load between contributing point, nonpoint, and natural background sources of pollutants in the watershed. Thus, water quality monitoring and other assessment activities are an integral part of the TMDL for a water body.

The particular parameter to be addressed under this QAPP is low dissolved oxygen in the lower 25 mile segment of Oso Creek, partially attributed to the runoff of nutrients applied to agricultural croplands. Specifically, efforts are underway to reduce nutrient loadings to Oso Bay, via the Oso Creek watershed, through implementation of agricultural best management practices (BMPs) under TSSWCB's Water Quality Management Plan (WQMP) program. Information generated from this and past projects will be useful in assessing surface water quality, developing TMDLs, and making permitting decisions.

Oso Bay is shallow, poorly circulated, and potentially sensitive to point and nonpoint source contributions of water-quality constituents. While sufficient data on urban runoff is available through the ongoing National Pollutant Discharge Elimination System (NPDES) study for the city of Corpus Christi, similar data on quantity and quality of agricultural runoff into Oso Bay is minimal. Because much of the area within the Oso Creek watershed is agricultural cropland, data on characteristics of cropland runoff would enable resource managers to assess the effectiveness of BMPs in reducing NPS loadings in the lower 25 mile segment of Oso Creek, and to modify or refocus cropland BMPs where necessary to reduce NPS loadings.

A6 Project/Task Description and Schedule

This project will characterize streamflows and water-quality constituent loadings (nutrients, major inorganic ions, sediments, and bacteria) emerging from two tributaries that drain agricultural watersheds in the Oso Creek basin during runoff events, and will assess the impact of agricultural practices applied in the two sub basins on water quality draining in the Oso Creek. The implementation of this project consists of the following tasks:

1. Establish a water-quality monitoring program to characterize the quantity and quality of surface runoff exiting the croplands sites within the watershed, and rainfall falling on the watershed.
2. Analyze the flow and water-quality data and calculate constituent loads and Event Mean Concentrations (EMCs) from storm events as well as annual loadings for each site.
3. Determine the annual loadings of nutrients applied to croplands by farmers in the two drainage areas and compare with annual loadings of constituents exiting the croplands through storm water runoff.

Task 1. Rainfall and Runoff Water-Quality Monitoring Program
Two surface water-quality monitoring stations installed for the preceeding TSSWCB Project 02-13 “Estimation of Water-Quality Constituents Loadings from Agricultural Croplands in the Oso Creek Watersheds” will be operated cooperatively by Research and the USGS. One station (Site 1, Figure A6) was installed on the upper reaches of West Oso Creek at County Road 30 draining approximately 5,145 acres of agricultural croplands. The other station (Site 2, Figure A6) was installed on a tributary to Oso Creek at County Road 2444 draining an estimated 5,287 acres of predominantly agricultural cropland. The data-collection platforms at each water-quality station are instrumented for the collection of rainfall, water stage, velocity, and discharge on a continuous basis. Data will be transmitted from each site by radio to the Geostationary Operational Environmental Satellite (GOES) on a near real-time basis and relayed, within minutes to the USGS internetpage (http://waterdata.usgs.gov/tx/nwis/rt). A rainfall sample collector also has been installed in the Oso Creek watershed at the Texas AgriLife Research and Extension Center at Corpus Christi (Site 3, Figure A6).

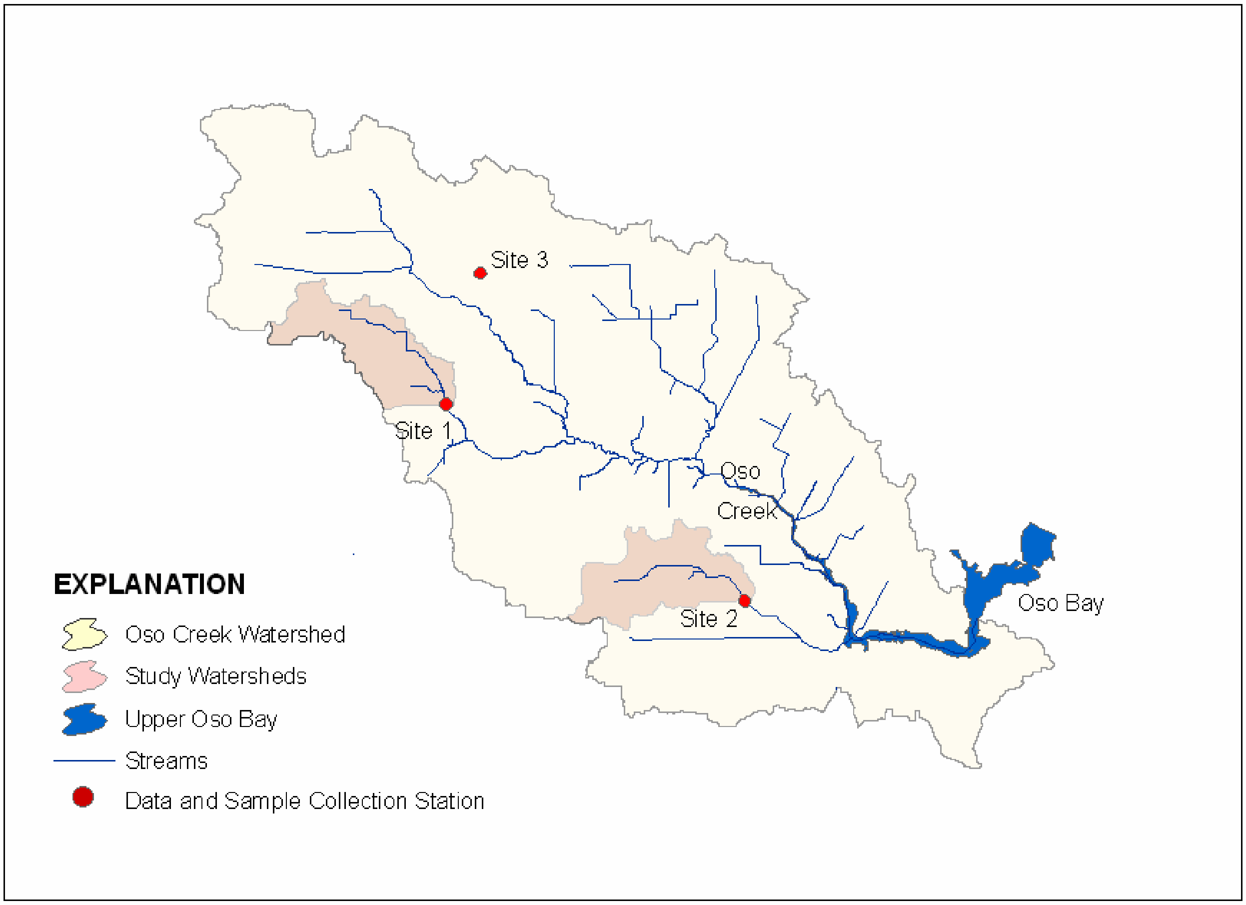


Figure A6. Location of Agricultural Study Watersheds in the Oso Creek Watershed

Because of the ephemeral nature of runoff at these sites, the stations are equipped with automatic samplers to collect water-quality samples during storm-events. At each station, during a runoff event, for the range of flow conditions, the automatic samplers will collect multiple, individual samples (aliquots) at regular timed intervals. At the end of the event the individual aliquots from each site will be combined into a single, composite sample for each site. During sample compositing, the individual aliquot volumes added to the composite sample will be weighted according to the stream discharge at the time the sample was collected. The volume of aliquot added to the composite sample will be proportional to the stream discharge. Thus, the final composite sample will be a discharge-weighted sample. The constituent concentrations of the discharge-weighted sample will represent the average discharge-weighted runoff concentrations during the runoff event. With this type of sampling protocol, the runoff loads (pounds) and yields (pounds per acre) of various constituents can be calculated by multiplying the constituent concentration of interest (for example, nitrate nitrogen) and the runoff volume (determined from the streamgage data).

Runoff samples will be analyzed by the USGS National Water Quality Laboratory (NWQL) for major ions and nutrients. The proposed analytes, including laboratory detection limits, are shown in Appendix A.

Runoff suspended sediment samples also will be collected at each station. The sediment samples will not be collected by automatic sampler but will be collected manually by equal increment, depth integrated method (USGS, 2002). Sediment samples will be analyzed by the USGS Sediment Laboratory in Iowa City, IA. Average event concentrations and loads of sediment will be calculated using regression equations that relate discharge and sediment concentration. Discrete grab samples will be collected at each site during storm runoff for bacterial analysis of fecal coliform, enterococci, and E. *coli* bacteria. The samples will be delivered to personnel from the TAMU-Corpus Christi (CC) environmental microbiology laboratory, under the direction of Joanna Mott.

The automatic rainfall sampler located in the Oso Creek watershed at the Texas AgriLife Research and Extension Center (Site 3, Figure A6) will collect rainfall samples that will be analyzed for nutrient concentrations. From rainfall nutrient sample concentrations and rainfall volumes, rainfall nutrient deposition (pounds per acre) to the study watersheds can be calculated. Rainfall samples also will be analyzed by the NWQL. The proposed nutrient analytes are listed in Appendix B. The rainfall samples will be collected during the events that produce runoff, if possible. Also, samples will be collected during several selected rainfall events that do not produce any runoff so that rainfall quality and rainfall deposition rates can be characterized for a range of rainfall events.

Depending on the occurrence of runoff events, about 3 samples will be collected from each runoff site, each year, for a total of 12 runoff samples. If possible, more samples will be collected, depending on occurrence of storms. For example, during FY06 and FY07, 9 and 10 runoff samples were collected, respectively. Also, if possible, the samples will be distributed between spring and fall events. Also, for a particular event, samples might only be collected from one site. Rainfall samples will be collected, if possible, during any event when runoff samples are collected. The numbers of runoff and rainfall samples, by fiscal year, are shown in the following table.

Fiscal Year	Runoff	Runoff-QA*	Rainfall	Rainfall-QA*
2006	9[a]	2[a]	9[a]	1[a]
2007	10[a]	2[a]	6[a]	1[a]
2008	3	1	4	1
2009	3	1	4	1
Total	12	4	13	2

[a] Actual number of samples for FY06-07(Oct 05 - Sept 07), under project #02-13, (revised Jan 08)
* quality assurance samples (duplicate-split samples or blank samples)

Task 2. Estimate Constituent Loadings and Event Mean Concentrations (EMCs)
The load of a chemical constituent may be defined as the product of the constituent concentration and the discharge and represents the total constituent mass that passes a point over a specified time period. Selected constituent loads and yields will be computed for each event, monthly, and annually. For sampled rainfall and runoff events, loads and yields will be computed directly from rainfall and runoff volumes and constituent concentrations:

$$\text{Load} = \text{EMC} \times \text{Volume} \times \text{Cf},$$

Where EMC is the event mean concentration, Volume is the runoff volume during the event (or, for rainfall loads, the rainfall volume on the watershed), and Cf is a conversion factor to produce load values in pounds. Yield is the load of constituent per acre of the contributing catchment study area.

For unsampled events, the mean or median concentration value determined from sampled events will be used along with measured rainfall and runoff volumes to estimate constituent loads and yields.

Task 3. Determine Annual Loadings of Nutrients Applied to Croplands

Farm producers within the two drainage areas will be identified with help from NRCS personnel. Farmers will be visited each year to record and quantify the nutrients used to produce each crop each year. These data and annual rainfall nutrient loadings will be used to quantify the total nutrient loadings on the acreage comprising the two study areas.

Subtasks are outlined in Table A6 along with a listing of responsible agencies and an activity schedule.

Table A6 Project Plan Milestones

Project Milestones	Agency	Start	End
Contact producers within each study site and arrange for collection of nutrient application data	Research, NRCS	Sep 07	Dec 08
Revise QAPP	Research, USGS	Sep 07	Feb 08
EPA approve QAPP	TSSWCB, EPA	Feb 08	Mar 08
Maintenance and calibration of automatic water quality samplers at sampling stations for the two contributing catchment study areas	Research, USGS	Jan 08	Aug 09
Obtain and analyze flow and water-quality data and calculate constituent loads and EMC from storm events	Research, USGS	Jan 08	Aug 09
Research and USGS submit draft final report to TSSWCB	Research, USGS		Aug 09
Research and USGS submit quarterly progress reports to TSSWCB	Research, USGS	Jan 08	Aug 09
Submit draft report	USGS, Research		Aug 09

Constraints in meeting this work schedule include timely approval of the QAPP and unexpected extreme variability in weather conditions that preclude sampling. See Section B1 for sampling design and monitoring pertaining to this QAPP.

A7 Quality Objectives and Criteria for Measurement Data

The objectives of the water quality monitoring implemented for this project are as follows:

1. To determine nonpoint source (NPS) pollution loadings into Oso Creek from agricultural croplands and to assess water quality parameters associated with BMPs for participating farms in the WQMP program.

2. To inform producers and policy makers of agricultural contributions to impairment of surface waters in the Oso Creek Watershed.

Water quality runoff and rainfall samples will be collected and analyzed for the presence of nutrients (various forms of nitrogen and phosphorus), major ions, and sediment associated with the production of crops within the study areas. These parameters will be measured because they are good indicators of water quality with respect to nutrient NPS pollution. The major data quality objective is to assess concentrations and loadings of nitrogen, phosphorus and major ions in surface water runoff from the BMPs implemented by producers through the WQMP program.

Samples will be analyzed if they meet preservation requirements and holding times. All samples will be analyzed within the estimated accuracy and precision limits of measured parameters to insure data quality. Table A7 lists QA objectives for water-quality measurement data. Documentation of NWQL methods for determination of analytical accuracy and precision is provided in Appendix C (USGS open file report 99-193), Appendix D (USGS fact sheet 023-98), and references listed in Table A7.

Database checks for validity will be performed on an on-going basis. Data will be reviewed by the USGS Quality Assurance Officer for abnormalities or any unusual results, e.g., a sample with a concentration of orthophosphate-phosphorus higher than the concentration of total phosphorus, prior to entry into the database. Any unusual results will be traced for error sources. In the event no error is found, the data will be assumed normal and appropriate for decision determinations. If an error is found and cannot be resolved, the data will be discarded.

The Project Manager/QA Manager will coordinate with the USGS Project Chief, USGS Quality Assurance Officer, and Research research staff to ensure that proper protocols are utilized. The USGS Project Chief and USGS Quality Assurance Officer will, in turn, coordinate with the NWQL and USGS Sediment Laboratory regarding discussions of protocol, questions about data, documentation of methods and results, and any necessary corrective actions.

The following text defines the recommended QA objectives for limit of quantitation, precision, bias, completeness, representativeness, and comparability of the data to be collected during the study.

Limit of Quantitation

The ambient water reporting limit (AWRL) set by TCEQ establishes the reporting specification at or below which data for a parameter will be reported for comparison with Texas Water Quality Standards. The AWRLs specified in Table A7.1 for each analyte should yield data acceptable for routine monitoring. The AWRL will be used as the limit of quantitation (LOQ) for all constituents. The laboratory will meet two requirements in order to report meaningful results in evaluating the project's objectives:

- The laboratory's reporting limit for each analyte will be at or below the AWRL.

- The laboratory will demonstrate and document on an ongoing basis the laboratory's ability to quantitate at its reporting limits.

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

Precision

Precision is a statistical measure of the variability of a measurement when a collection or an analysis is repeated and includes components of random error. It is strictly defined as the degree of mutual agreement among independent measurements as the result of repeated application of the same process under similar conditions. Laboratory precision is assessed by comparing replicate analyses of laboratory control standards in the sample matrix (e.g., deioinized water) or sample/duplicate pairs in the case of bacterial analysis. Precision results are plotted on quality control charts that are based on historical data and used during evaluation of analytical performance. Performance specifications for laboratory control standard/laboratory control standard duplicate pairs are defined in Table A7.1. Field splits are used to assess the variability of sample handling, preservation, and storage, as well as the analytical process, and are prepared by splitting samples in the field. Control limits for field splits are defined in Section B5.

Precision of laboratory analytical data will be evaluated by:

1. Laboratory control samples (LCS) – the NWQL analytical systems analyze one or more of a series of reference samples, including standard reference samples, surrogate spikes, certified reference materials, surrogate spikes, and continuing verification standards. The LCS are used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The number of LCS samples can vary and is either specified in the method or SOP. Data from the LCS are compared to established criteria, and, if found to be outside of the criteria, indicate that the analytical system is out of specification. Any affected samples associated with an out-of-specification LCS are reanalyzed or the results reported with appropriate data-qualifying codes. (Appendix F - NWQL QMS, section A.1.1)

Bias

Bias is a statistical measurement of correctness and includes multiple components of systematic error. A measurement is considered unbiased when the value reported does not differ from the true value. Bias is verified through the analysis of laboratory control standards prepared with verified and known amounts of analytes and by calculating percent recovery. Results are plotted on quality control charts and used during evaluation of analytical performance. Project control limits for laboratory control standards are specified in Table. A7.1.

Bias of field measurements (specific conductance and pH) will be evaluated by:

1. Standard methods - measurement methods will be used which are recognized and considered standard by the scientific community. (USGS, QAPP, Appendix E)
2. Calibration and calibration checks of field instruments and equipment will be performed at a frequency that ensures each measurement is accurate. (USGS, QAPP)

Bias of laboratory analytical data will be evaluated by:

1. Standard methods - analysis methods will be used which are recognized and considered standard by the scientific community. (NWQL, QMS, Appendix F)

2. Calibration standards - primary standards will be obtained from the National Institute of Standards and Technology (NIST), USEPA repository, or other reliable commercial source. (NWQL, QMS)

3. Blind Sample Program - the USGS Branch of Quality Systems manages the Inorganic Blind Sample Project to submit blind samples to the NWQL to assess the entire analytical range of most organic-analyte determinations. The purpose of this project is to produce an independent, third party evaluation of the quality of data from the NWQL. (NWQL, QMS, section A.2.5).

4. Laboratory set and surrogate spikes - results are compared to the acceptance criteria as published in the mandated test method. Where there are no established criteria, the NWQL determines internal criteria and documents the method to establish the limits (NWQL, QMS, section A.1.1.2).

<u>Completeness</u>

The completeness of the data is basically a relationship of how much of the data is available for use compared to the total potential data. 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.

Completeness of field data will be evaluated by:

1. All measurements and observations will be recorded on appropriate USGS field sheets as shown on pp 42, 43 of the USGS QAPP, Appendix E.

2. All deviations from standard USGS procedures will be recorded and documented.

Completeness of laboratory analytical data will be evaluated by:

1. Each data set (batch) shall contain all QC check analyses verifying precision and accuracy for the analytical protocol.

2. All pertinent dates are to be recorded (receive date, analyze date, etc.)

3. All requested analyses will be performed or documentation provided as to the reason for non-performance.

4. All nutrient parameters for runoff and rainfall samples and major ions in runoff samples must be within the lab reporting limits in Table A7.

Table A7 Quality Assurance Objectives for Measurement Data

PARAMETER	UNITS	MATRIX	METHOD	STORET CODE	Lab Reporting Limit (LRL)	LAB
Field Parameters						
Specific Conductance	µS/cm	Water	USGS - NFM	00095	NA	NA
pH	Std units	Water	USGS - NFM	00400	NA	NA
Temperature	Deg C	Water	USGS - NFM	00010	NA	NA
Nutrients (runoff samples)						
Nitrogen, ammonia, dissolved	mg/L	Water	USGS I-2522-90	00608	0.04	NWQL
Nitrogen, ammonia + organic nitrogen, dissolved	mg/L	Water	USGS I-2515-91	00623	0.10	NWQL
Nitrogen, ammonia + organic nitrogen, total	mg/L	Water	USGS I-4515-91	01005	0.10	NWQL
Nitrogen, nitrite, dissolved	mg/L	Water	USGS I-2540-90	00613	0.008	NWQL
Nitrogen, nitrite + nitrate, diss.	mg/L	Water	USGS I-2545-90	00631	0.06	NWQL
Phosphorus, dissolved	mg/L	Water	EPA 365.1	00666	0.004	NWQL
Phosphorus, total	mg/L	Water	EPA 365.1	00665	0.004	NWQL
Phosphorus, phosphate, ortho	mg/L	Water	USGS I-2601-90	00671	0.018	NWQL
Nutrients (rainfall samples)						
Nitrogen, ammonia, dissolved	mg/L	Water	USGS I-2525-89	00608	0.01	NWQL
Nitrogen, ammonia + organic nitrogen, dissolved	mg/L	Water	USGS I-2515-91	00623	0.10	NWQL
Nitrogen, ammonia + organic nitrogen, total	mg/L	Water	USGS I-4515-91	01005	0.10	NWQL
Nitrogen, nitrite, dissolved	mg/L	Water	USGS I-2542-89	00613	0.002	NWQL
Nitrogen, nitrite + nitrate, diss.	mg/L	Water	USGS I-2546-91	00631	0.016	NWQL
Phosphorus, dissolved	mg/L	Water	EPA 365.1	00666	0.004	NWQL
Phosphorus, total	mg/L	Water	EPA 365.1	00665	0.004	NWQL
Phosphorus, phosphate, ortho	mg/L	Water	USGS I-2606-89	00671	0.006	NWQL
Major Ions (runoff samples)						
Calcium, dissolved	mg/L	Water	USGS I-1472-87	00915	0.02	NWQL
Chloride, dissolved	mg/L	Water	USGS I-2058-89	00940	0.01	NWQL
Fluoride, dissolved	mg/L	Water	USGS I-2058-89	00950	0.01	NWQL
Magnesium, dissolved	mg/L	Water	USGS I-1472-87	00925	0.008	NWQL
Potassium, dissolved	mg/L	Water	STD MET 3120 – ICP	00935	0.01	NWQL
Silica, dissolved	mg/L	Water	USGS I-1472-87	00955	0.04	NWQL
Sodium, dissolved	mg/L	Water	USGS I-1472-87	00930	0.20	NWQL
Sulfate, dissolved	mg/L	Water	USGS I-2058-89	00945	0.01	NWQL

References:
USGS NFM – U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chapters A1-A-9, available online at http://pubs.water.usgs.gov/twri9A
EPA 365.1 – Determination of Phosphorus by Semi-Automated Colorimetry Revision 2.0, Methods for the Determination of Inorganic Substances in Environmental Samples
USGS I – 1472-87, I-2525-89, I – 2522-90, I-2540-90, I-2542-89, I-2545-90, I-2546-91, I-2601-90 I-2606-89 - Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.
USGS I – 2515-91 - Patton, C.J., amd Truitt, E.P., 2000, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of ammonium plus organic nitrogen by a Kjeldahl digestion method and an automated photometric finish that includes digest cleanup by gas diffusion: U.S. Geological Survey Open-File Report 00-170, 31 p.
USGS I – 2058-89 - Fishman, M.J., and Friedman, L.C., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.
STD MET - 3120 – ICP – American Public Health Association, 1998, Standard methods for the examination of water and wastewater (20th ed.); Washington, D.C., American Public HealthAssociation, American Water Works Association, and Water Environment Federation, p.3-37 - 3-43.

Representativeness

The data collected as routine grabs and storm samples will be considered representative of the target population or phenomenon to be studied. The representativeness of the data is dependent on 1) the sampling locations, 2) the flow regime during sample collection 3) the number of years sampling is performed, and 4) the sampling procedures. Site selection and sampling of pertinent media (i.e., water) and use of only approved analytical methods will assure that the measurement data represent the population being studied at the site. Although data may be collected during varying regimes of weather and flow, data collection will be targeted toward both ambient conditions and storm events, representing water quality at high and low flow conditions. The goal for meeting total representation of the water body will be tempered by the funding available.

.***Representativeness of field data will be evaluated by:***

1. Use of standard USGS methods of measurement and sample collection.

2. Documentation of non-standard techniques.

Representativeness of laboratory analytical data will be evaluated by:

1. Use of preservation techniques (including chilling during shipment of samples) to minimize sample degradation which may occur between sample collection and analysis.

2. Prescribed holding times shall be adhered to by the analytical laboratory.

Comparability

Confidence in the comparability of data sets for this project is based on the commitment of project staff to use only approved sampling and analysis methods and QA/QC protocols in accordance with quality system requirements and as described in this QAPP. Comparability is also guaranteed by reporting data in standard units, by using accepted rules for rounding figures, and by reporting data in a standard format as specified in Section B10 on Data Management.

Comparability of field measurements and laboratory analytical data will be evaluated by:

1. Standard methods - measurement methods shall be used which are recognized and considered as standard by the scientific community.

2. Reporting units - data shall be reported in units specified by USEPA or USGS analytical methods.

A8 Special Training Requirements/Certification

The USGS NWQL has obtained NELAP Laboratory accreditation, effective December 5, 2007 through December 31, 2008 in accordance with Texas Water Code Chapter 5, Subchapter R, Title 30 Texas Administrative Code Chapter 25, and the Mational Environmental Laboratory Accreditation Program. A copy of the accreditation certificate is included in Appendix I.

A9 Documentation and Records

Hard copies of all field data sheets and general maintenance (GM) records for field equipment, will be archived by Texas AgriLife Research and Extension Center at Corpus Christi for at least five years. Records applicable to the NWQl, including electronic copies and/or hard copies of all general maintenance (GM) records for laboratory equipment, chain of custody forms (COCs), laboratory data entry sheets, calibration logs, and laboratory corrective action reports will be archived by the NWQL. In addition, Research and USGS will archive electronic forms of all project data for at least five years. USGS data storage, backup, and records archival practices and policies are detailed in sections 10.3 (Data Storage) and 10.4 (Records Archival) of The USGS Texas Quality Assurance Plan for Water-Quality Activities in the Texas District (Appendix E).

Quarterly progress reports will be generated by Research and USGS and will note activities conducted in connection with the water quality monitoring program, items or areas identified as potential problems, and any variations or supplements to the QAPP. Any changes or variations from the QAPP will be made known to pertinent project personnel and documented in an update or amendment to the QAPP. All quarterly progress reports and QAPP revisions will be distributed to personnel listed in Section A3 by Research. Research and USGS will also be responsible for submitting the final report for this project.

Laboratory Documentation

The laboratory will document sample results clearly and accurately. Information about each sample will include the following to aid in interpretation and validation of data:

- A clear identification of samples analyzed for the project including station information
- Date and time of sample collection
- Identification of preservation and analysis methods used
- Sample results, units of measurement, and sample matrix
- Information on QC failures or deviations from requirements that may affect the quality of results or is necessary for verification and validation of data

Revisions to the QAPP

Until the work described is completed, this QAPP shall be revised as necessary and reissued annually on the anniversary date, or revised and reissued within 120 days of significant chamges, whichever is sooner. If the entire QAPP is current and valid, the document may be reissued by certifying that the plan is current and including a new copy of the signed approval page. The approved version of the QAPP shall remain in effect until revised verswions have been approved, only if the revised version is submitted for approval before the approved version expires.

Expedited Changes

Expedited changes to the QAPP should be approved before implementation to reflect changes in project organization, tasks, schedules, objectives, and methods, address deficiencies and nonconformance, improve operational efficiency and accommodate unique or unanticipated circumstances. Requests for expedited changes are directed from the Texas AgriLife Research and Extension Center Project Manager to the TSSWCB Project Manager in writing. They are effective immediately upon approval by the TSSWCB Project Manager and Quality Assurance Officer, or their designees, and the EPA Project Manager.

Justification, summaries, and detals of expedited changes to the QAPP will be documented and distributed to all persons on the QAPP distribution list under the direction of the Texas AgriLife Research and Extension Center QAO. Expedited changes will be reviewed, approved, and incorporated into a revised QAPP during the annual revision process or within 120 days of the initial approval in cases of significant changes.

The documents and records that describe, specify, report, or certify activities are listed in Table A9.

Table A9 Project Documents and Records

Document/Record	**Location**	**Retention (yrs)**	**Format**
QAPPs, amendments and appendices	Research Offices	5 years	Electronic
QAPP, distribution documentation	Research Offices	5 years	Electronic
Field training records	Research, USGS, TAMU Field Offices	5 years	Electronic/paper
Field notebooks or data sheets (see Appendix B for examples of field data sheets)	Research Offices	5 years	Paper
Field equipment calibration/maintenance logs	Research, USGS, TAMU Field Offices	5 years	Electronic/paper
Field instrument printouts	Research, USGS, TAMU Field Offices	5 years	Paper
Field SOPs	Research, USGS, TAMU Field Offices	5 years	Paper
Chain of custody records (see Appendix C for example)	TAMU-CC laboratory	5 years	Paper
Laboratory Quality Manuals	USGS, TAMU-CC Laboratories	5 years	Paper
Laboratory training records	USGS, TAMU-CC Laboratories	5 years	Electronic/paper
Laboratory SOPs	USGS, TAMU-CC Laboratories	5 years	Paper
Laboratory instrument printouts	USGS, TAMU-CC Laboratories	5 years	Paper
Laboratory data reports/results	TIAER Laboratory or Offsite Storage	5 years	LIMS electronic/paper
Laboratory equipment maintenance logs	USGS, TAMU-CC Laboratories	5 years	Electronic/paper
Laboratory calibration records	USGS, TAMU-CC Laboratories	5 years	LIMS electronic
Corrective Action Documentation (see Appendix D for example)	Research Office	5 years	Electronic/ Paper

The TSSWCB may elect to take possession of records (or copies thereof) at the conclusion of the specified retention period.

B1 Sampling Process Design

This project is designed to estimate the loadings of nutrients, sediment, and selected inorganic ions in stormwater runoff originating from croplands in the lower 25 mile segment of Oso Creek, as described in Section A6. The sample design is based on the program requirements of the TMDL Program.

Water samples will be collected from each stormwater runoff event and analyzed for the presence of all forms of nitrogen and phosphorus, sediment, and selected inorganic ions. In addition, rainfall samples will be collected and analyzed for nutrient concentrations. A complete listing of the nutrient and ion constituents that will be measured are shown in Appendix A for runoff samples and Appendix B for nutrients in rainfall samples.

Sample collection will commence when equipment has been installed at the sampling sites and when rainfall produces storm water runoff from the contributing cropland areas. If possible, each rainfall event that produces storm water runoff will be sampled. A Research research technician will serve as the field technician along with the USGS Project Chief and support personnel from San Antonio and will transport field samples from the sampling sites, and properly prepare the field samples (described in Section B3) for overnight shipment to the NWQL and the USGS Sediment Laboratory.

B2 Sampling Method Requirements

Water Quality Field Sampling Procedures

All field sampling will follow appropriate protocols set forth in Section 6 of the *USGS Texas Quality Assurance Project Plan for Water Quality Data Collection Activities in the Texas District, Appendix E*. The samples will be collected at the two streamflow and sampling stations as described in Section A6.

One set of samples will be timed samples (aliquots) collected by automatic samplers during runoff events. The aliquots will be discharge-weighted and composited and analyzed as single samples (single composite sample from each site, during a runoff event). All nutrient and ion constituents will be analyzed from these samples.

A portion of the composited (discharge-proportional) sample will be sent to the NWQL for the following analyses:

- Nitrate + Nitrite Nitrogen
- Ammonia Nitrogen
- Total and dissolved Kjeldahl Nitrogen
- Total and dissolved Phosphorus
- Orthophosphorus
- Trace Elements – Calcium, Chloride, Sodium, Sulfate, Potassium, etc.

The rainfall samples will be analyzed for dissolved and total forms of nitrogen and phosphorus, and orthophosphorus (Appendix B). Specific conductance and pH, will be measured for each composite sample. These measurements will be made at the Research lab. Sample volumes, container types, and preservation requirements are also provided in Appendix A and Appendix B.
A second set of runoff samples for suspended sediment will be collected at each station. The sediment samples will not be collected by automatic sampler but will be collected manually by equal increment, depth integrated method (http://tx.cr.usgs.gov/field/plans/qwqaplan.pdf). Sediment samples will be analyzed by the USGS sediment laboratory in Iowa City, IA. From the sediment sample concentrations, regression equations that relate discharge and sediment concentration will be developed to calculate average event concentrations and sediment loads and yields.

Water-quality samples will be collected from the field immediately following a rainfall and/or storm runoff event, prepared, and shipped overnight to the laboratories for analyses.

During runoff events, discharge measurements will be made at each station to develop stage-velocity-discharge ratings. The ratings will be used to compute stream discharge from the measurements of stage, or water elevation and water velocity. Discharge measurements will be made at each site in accordance with normal USGS streamgaging practices. The number of discharge measurements made at each station will depend upon the number of storm events and flow characteristics of the watersheds. All rainfall and streamflow records will be maintained in the USGS National Water Information System (NWIS) data base.

Processes to Prevent Contamination

Cleaning/decontamination of automatic samplers will be conducted according to guidelines specified in section 6.3.4 of Appendix E (USGS QAPP pp 15-16). Field and laboratory equipment used for processing field samples (churns, pumps, tubing) will be decontaminated according to section 6.3.7 of Appendix E, pp. 17-18.

Byproducts of cleaning and decontamination include methanol, hydrochloric acid solution, and soap solution. These waste byproducts will be collected and transported to the USGS San Antonio Water Science Center and disposed of in accordance with chemical waste disposal instructions described in the USGS Chemical Hygiene Plan.

All equipment and support facilities needed to carryout the sampling activities, prepare samples in the laboratory and ship overnight to the USGS Laboratories will be provided by USGS and Research.

Water Quality Sample Collection Logistics During Runoff Events

A description of the logistics of mobilizing manpower and collecting streamflow data and waterquality samples during a storm-runoff event is given below.

1. USGS personnel in San Antonio have access to forecasting and real-time data, and so will be aware of potential runoff events. The rainfall and flow data at the Oso Creek sites will be accessible by satellite-internet link. USGS will try to anticipate events in order to be prepared to travel and arrive at the sites as soon as possible.

2. Research will also have advance warning and will be contacted by beeper when flow starts to occur at the sites.

3. Research will send a technician to the sites during a runoff or rainfall event.

4. Since both streamflow sites can be monitored by satellite-internet link, each site can be monitored to determine which site should be visited first. It is possible that one site may not flow while the other flows during the same event. There could also be time lags between events at the two different stations. Also, as the study progresses, one station may have very little data compared with the other site. So the site with little data may become the priority site. During an event, a station can be monitored from the other station so that the progress of each station during the storm can be observed and personnel dispatched to make measurements and collected samples as needed.

5. While in transit from San Antonio, USGS will be in contact with Research to determine a priority site. If samples are already being collected by autosampler at one of the sites, Research can likely be on location first and collect samples as needed.

6. USGS will make all discharge measurements. Research personnel will concentrate on sample collections and handling. Event conditions will dictate where discharge measurements are made. Typically, during an event, both sites will be visited quickly to ensure that automatic samplers and gaging equipment are operating properly. Then discharge measurements and sediment sampling will be performed.

7. The two stations will be set up so that sample aliquots will be collected beginning within 1 hour after flow begins. The aliquots will be collected at a timed rate (for example, hourly). The samplers will be programmed so that the sample bottles will be filled after about 12 hours of runoff sampling. Runoff events lasting more than 12 hours will require replacement of the auto-sampler bottles for continued sampling. Spare sample jars (cleaned, rinsed with methanol, and sealed) will be available. The first set of samples will be stored (chilled) and set aside to combine with the next set of samples. When the next set of samples is collected, they will be included with the first set of samples in the compositing process.

   Each sample jar will include a clean lid (the lids are to be stored in plastic bags) and each individual jar will be labeled before transport back to the Research lab. All of these samples must be composited in the Teflon coated churn which is in the Research lab.

8. All samples are to be properly labeled in the field before transport to the Research lab. Each person involved in sample collection will have ice chests available for storing and transporting the samples. All samples will be taken to Research for initial processing. Timed-auto samples will be composited in the Teflon churn. The churn is to be cleaned using USGS QAPP procedures between each set of samples. Specific conductance and pH will be measured for each composite sample. USGS personnel will oversee the sample processing in the Research lab. USGS will also provide labels for all samples and the necessary shipping forms for the NWQL lab and the USGS Sediment Laboratory.

9. For a major storm, sample collection, processing, and delivery may extend over 48 hours.

Documentation of Field Sampling Activities

Field sampling activities are documented on USGS field sheets (pp 42, 43) as presented in the USGS QAPP (Appendix E). All sample information will be logged into a field log. The following will be recorded for all sampling:

- Station ID/location
- Date
- Sampling time
- Sample type
- Bottle number for timed samples and collection time
- Sample collector's name/signature
- COC number

Upon collection, all samples will be transported in an iced container to the Research laboratory for preparation and shipment (described in Section B3) to the NWQL and the Iowa Sediment Laboratory. All filtration and preservation, other than the temperature reduction by ice, will be performed in the Research laboratory.

Recording Data

For the purposes of this section and subsequent sections, all field personnel follow the basic rules for recording information as documented below:

1. Legible writing with no modifications, write-overs or cross-outs
2. Correction of errors with a single line followed by an initial and date
3. Close-outs on incomplete pages with an initialed and dated diagonal line.

Additional requirements pertaining to NWQL document management and record keeping are found in Appendix F – NWQL QMS, section 2.3.

Deficiencies, Nonconformances and Corrective Action Related to Sampling Methods Requirements

Deficiencies are defined as unauthorized deviations from procedures documented in the QAPP. Noncomformances are deficiencies that affect quality and render data unacceptable or indeterminate. Examples of failures in sampling methods and/or deviations from sample design requirements include but are not limited to such things as sample container problems, inadequate sample volume due to spillage or container leaks, contamination of a sample bottle during collection, failure to preserve samples appropriately, storage temperature and holding time exceedance, and sample site adjustments Any deviations may require corrective action. Deficiencies are documented in logbooks and field data sheets by field or laboratory staff and reported via Corrective Action Report (CAR) to the pertinent field or laboratory supervisor. The supervisor will forward the CAR to the QAM. Corrective action may require samples to be discarded and re-collected. It is the responsibility of the Research Project Leader, in consultation with the Research QAM and the USGS Project Chief to ensure that the actions and resolutions to the problems are documented and that records are maintained in accordance with the QAPP. The Research Project Leader, Research QAM, USGS Project Chief, and TSSWCB, QAM, will determine if the deviation from the QAPP compromises the validity of the resulting data. The Project Leader, in consultation with the Research QAM, the USGS Project Chief, and TSSWCB QAO will decide to accept or reject data associated with the sampling event, based on best professional judgment. A CAR will be retained by the QAM and resolution of the situation will be reported to the TSSWCB in the quarterly report.

Corrective Action Reports (CARs) document: root cause(s); programmatic impact(s); specific corrective action(s) to address the deficiency; action(s) prevent recurrence; individual(s) completion of each corrective action will be documented. Significant conditions (i.e., situations that, if uncorrected, could have a serious effect on safety or validity or intergrity of data) will be reported to the TSSWCB immediately.

B3 Sample Handling and Custody Requirements

Sample Holding Times

The NWQL Laboratory Information Management System (LIMS) tracks time-critical processes for each sample, including time of collection, login date, sample preparation date, analysis date, and the release date to the customer (project manager, QA officer, etc). The maximum holding times from the time of sampling are summarized below:

Ammonia-Nitrogen .... 30 days
Nitrate-Nitrogen .... 30 days
Nitrogen, Total Kjeldahl .... 30 days
Nitrogen, Total Organic .... 30 days
Nitrite-Nitrogen... 30 days
Ortho Phosphate .... 30 days
Total Phosphate/Phosphorus .... 30 days
Sulfur/Sulfate .... 180 days
Boron... 180 days
Iron .... 180 days

Table 3.1 in Appendix F (USGS NWQL QMS) includes references/sources for holding time determinations.

Chain-of-Custody

Proper sample handling and custody procedures ensure that the custody and integrity of samples beginning at the time of sampling and continuing through transport, sample receipt, preparation, and analysis. The USGS Analytical Service Request (ASR) serves as a chain-of-custody form and is used to document sample handling during transfer from the field to the NWQL and sediment laboratories. USGS chain-of-custody procedures for field collection of water samples and laboratory custody procedures are given in Section 7 of the USGS QAPP (Appendix E). A copy of the ASR-COC form is located on page 79 in Appendix E.

The NWQL is a restricted access facility that uses a proximity card system for employee entry. The NWQL is located on the Denver Federal Center (DFC) campus. The DFC protocols require all employees and visitors to pass through guarded gates. Visitors must sign in at the NWQL reception desk and be escorted by an NWQL employee at all times. Samples received at the NWQL are promptly logged into the electronic Laboratory Information Management System (LIMS). These samples are then checked for proper preservation (if required) and placed in storage areas appropriate for each sample type to await analysis. No further security procedures are involved. Samples are disposed of after normal holding times using routine disposal procedures. At the end of each business day the LIMS sends an email to the USGS San Antonio QA officer detailing conditions of samples received. The system acknowledges receipt and login of the samples at the NWQL, as well as any problems with the structural integrity of the sample containers and the shipping container.

Sample Labeling

All sample containers will be labeled with an indelible, waterproof marker at the site and transported to the Research lab by Research and USGS personnel. The following minimum information will be entered on the same label:

Station ID
Date
Time
Sample Type - Grab (sediment) or Timed autosample
For timed samples include bottle number (e.g. 1 of 3) and collection time
Preservative (if applicable)

Sample Handling

Following collection, samples are placed on ice in an insulated cooler for transport to the Research laboratory. Timed samples will be composited by USGS and Research personnel at the Research lab. The composited sample will be bottled for shipment to the NWQL. The sediment samples will be bottled for shipment to the USGS Sediment Laboratory.

The samples bound for NWQL will be packed in insulated shipping containers with ice and "bubble wrap". Samples brought in from the field and awaiting processing will remain on ice inside coolers or stored in the Research lab refrigerator. Sample containers, preservatives, and shipping instructions are included in appendices A and B. Sediment samples are not chilled and require no preservatives.

Samples and their containers will be kept under surveillance of the sampling team or in a secure storage area until transfer to the shipping agent. Each container will be secured with a custody seal showing the sampler's signature and date of transfer to the shipper. Samples will be shipped via overnight delivery.

Deficiencies, Nonconformances and Corrective Actions Related to Chain-of-Custody

All failures associated with chain-of-custody procedures, as described in this QAPP, are immediately reported to the Research Project Manager/QA Manager. These include such items as delays in transfer, resulting in holding time violations; violations of sample preservation requirements; incomplete documentation, including signatures; possible tampering of samples; broken or spilled samples, etc.

The Research Project Manager/QA Manager in conjunction with the USGS Project Chief and the TSSWCB QAM will determine if the procedural violation may have compromised the validity of the resulting data. Any failures that potentially compromise data validity will invalidate data, and the sampling event should be discarded. The resolution of the situation will be reported to the TSSWCB in the quarterly progress report. Corrective action reports will be maintained by the Research Project Manager/QA Manager. Significant conditions (i.e., situations that, if uncorrected, could have a serious effect on safety or validity or intergrity of data) will be reported to the TSSWCB immediately.

B4 Analytical Methods Requirements

The parameters listed in Appendix A and Appendix B will be analyzed by the USGS NWQL in Denver, CO. A listing of analytical methods is provided in the tables. Standard operating procedures have been established for all procedures undertaken by staff that concerns sample monitoring and analysis. The NWQL Quality Management System (Appendix F) provides detailed procedures.

Analytical support equipment includes balances, refrigerators, freezers, temperature measuring devices, and volumetric-dispensing devices. Support equipment is maintained in proper working order. The equipment is calibrated or verified at least annually, using NIST traceable references when available, for the entire analytical range. Section 3.4 of the NWQL Quality Management System (Appendix F) provides more details.

Deficiencies, Nonconformances and Corrective Actions Related to Analytical Methods

In the event of an unresolved, systemic failure in the Laboratory analytical system, the Research Project Manager/QA Manager will be notified, through communication with USGS project personnel. The Project Manager/QA Manager, the USGS Project Chief, and the TSSWCB QAM will then determine if the existing sample integrity is intact, or if the data should be omitted. The situation and agreed resolution will be reported to the TSSWCB in the quarterly progress report.. Significant conditions (i.e., situations that, if uncorrected, could have a serious effect on safety or validity or intergrity of data) will be reported to the TSSWCB immediately.

B5 Quality Control Requirements

The use of approved sampling and analytical methods will ensure that measured data accurately represent conditions at each monitoring site. The completeness of the data will be affected by the reliability of the equipment, frequency of field and laboratory errors or accidents, and unexpected events; however, the general goal requires 90 percent data completion.

Research/USGS sampling site audits, and quality assurance of field sampling methods will be conducted by the Research QA Manager. In addition, laboratory audits, sampling site audits, and quality assurance of field sampling methods will be conducted by the TSSWCB QAO or their designee at their discretion.

It is the responsibility of the Research Project Manager and the USGS Project Chief to verify that the data are representative. Acceptance of the chemistry data precision, accuracy, and comparability will be the responsibility of the USGS Project Chief and Quality Assurance Specialist. The Research Project Manager has the responsibility of determining that the 90 percent completeness criteria is met, or will justify acceptance of a lesser percentage. All incidents requiring corrective action will be documented and maintained by the Research Project Manager and the TSSWCB Project Manager.

The USGS NWQL and sediment laboratories use documented methods for determination of inorganic substances and sediment in water. The methods used include methods approved by the USGS, USEPA, the American Water Works Association, the Water Environmental Federation, or the ASTM.

Quality-control procedures for water-quality samples are explained below under their respective headings.

Research/USGS Sampling Quality Control Requirements and Acceptability Criteria

Equipment blanks – After installation of autosampler equipment at both sites, equipment blank samples will be collected to ensure that the equipment is not a source of contamination. Equipment blanks will be collected by pumping blank water through the sampler tubing line, autosampler, and autosampler jars. Equipment blank analysis will be done by NWQL.

Field Splits – A field split is a single sample subdivided by field staff immediately following collection. Field splits are submitted to the NWQL as two separate, identified samples. Split samples are preserved, handled, shipped, and analyzed identically and are used to assess variability in all of these processes. The precision of field split results is calculated by relative percent difference (RPD) using the following equation:

$$\mathbf{RPD = \{ (X_1 - X_2) / (X_1 + X_2)/2\} * 100}$$

A 20% RPD criteria will be used to screen field split results as a possible indicator of excessive variability in the collection and analytical system. Field splits will be collected at a frequency of 25%. Professional judgment will be used to determine the acceptability of field split analyses. During the study, selected composite samples will be subdivided into two split samples and analysis of both samples will be compared to precision goals.

No field spikes are planned for the study. The USGS NWQL incorporates laboratory control samples (standard reference samples, reagent spikes, surrogate spikes) as part of the laboratory QC sample program (USGS NWQL QMS).

The phase I data collection period listed 24 months, from October 2005 to September 2007. Nineteen runoff samples were collected during phase I. During phase II (September 2007 to March 2009) a total of about 12 runoff samples are planned, depending on hydrologic conditions and occurrence of runoff events.The breakdown of sample types is:

1 set of equipment blanks at each station —	2 samples
12 runoff samples from the two stations —	12 samples
Total —	14 samples

Unsampled events (if any) will have available rainfall and streamflow data. Average, median, or seasonal estimates of EMCs based on samples collected during other events can be used to estimate constituent runoff loads during unsampled events. During the first quarter of FY2008 a USGS report will be prepared describing the results of the phase I data collection. During the last quarter of FY 2009 a a USGS report will be prepared describing the results of the phase II data collection.

NWQL Measurement Quality Control Requirements and Acceptability Criteria

Detailed laboratory QC requirements are contained within each individual method and NWQL standard operating procedures (SOPs) . NWQL QC sample results are reported with the laboratory data report. NWQL SOPs QAMs are available upon request.

TAMU-CC Environmental Microbiology Laboratory Measurement Quality Control Requirements and Acceptability Criteria

Analyses to determine bacteria concentrations will be performed by the TAMU-CC Environmental Microbiology Laboratory. Laboratory QC requirements are contained within laboratory SOPs and in the laboratory Quality Manual. The minimum requirements for laboratory quality control are stated below.

Laboratory Duplicate – Laboratory duplicates are used to assess precision. Precision is calculated by the relative percent difference (RPD) of duplicate results as defined by 100 times the difference (range) of each duplicate set, divided by the average value (mean) of the set. For duplicate results, X_1 and X_2, the RPD is calculated from the following equation:

$$\mathbf{RPD = (X_1 - X_2) / \{(X_1 + X_2)/2\} * 100}$$

A bacteriological duplicate is considered to be a special type of laboratory duplicate and applies when bacteriological samples are run in the field as well as in the laboratory. Bacteriological duplicate analyses are performed on samples from the sample bottle on a 10% basis. Results of bacteriological duplicates are evaluated by calculating the logarighm of each result and determining the range of each pair.

Performance limits and control charges are used to determine the acceptability of duplicate analyses. Precision limits for bacteriological analyses are defined in Appendix G and applies to all samples with concentrations > 10 organisms/100 ml.

Laboratory Control Standard (LCS/Laboratory Control Standard Duplicate (LCSD) – (not applicable)

Matrix Spike (MS) – (not applicable)

AWRL/Reporting Limit Verification – The laboratory's reporting limit will be at or below the AWRL. (Verification not applicable)

Laboratory Equipment Blank – (not applicable)

Method Blank – A method blank is an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing and analyzed with each preparatory and analytical batch. The equivalent quality control for bacteriological membrane filtration methods follows TCEQ *Surface Water Quality Monitoring Procedures Volume 1: Physical and Chemical Monitoring Methods for Water, Sediment and Tissue* (December, 2003). For each membrane filter test, sterility of the media, petri dishes, membrane filters, dilution water, and apparatus will be checked using about 20 ml sterile water. If colonies appear on the blank, then all data from samples filtered after the blank will be discarded. A blank is run at the start and end of each group of samples analyzed. In cases where extremely high levels of bacteria are present in the sample, the blank run at the end of the group should have less than 1% of the colonies on the sample filter. Corrective action will be implemented if these values are exceeded.

Additional method-specific QC requirements – Additional QC samples are run (e.g., positive controls, negative controls) as specified in Section 9020 B, *Standard Methods for the Examination of Water and Wastewater* (20^{th} Edition, 1998).

Deficiencies, Nonconformances and Corrective Actions Related to Quality Control Requirements

In that differences in field duplicate sample results are used to assess the entire sampling process, the arbitrary rejection of results based on pre-determined limits is not practical. Therefore, the professional judgment of the Research Program Manager, USGS Project Chief, NWQL Laboratory staff, and QAO will be relied upon in evaluating results. Rejecting sample results based on wide variability is a possibility. Notations of field duplicate excursions and blank contamination are noted in the quarterly report to Research and in the final QC Report. .. Significant conditions (i.e., situations that, if uncorrected, could have a serious effect on safety or validity or intergrity of data) will be reported to the TSSWCB immediately.

When conditions in sampling or analysis are shown to be in error or in any way unsatisfactory, a corrective action will be employed incorporating the following steps:

1. Define the problem
2. Assign responsibility
3. Investigate and determine the cause of the problem
4. Determine a corrective action to eliminate the problem
5. Assign and accept responsibility for implementing the corrective action
6. Establish effectiveness of the corrective action and implement the correction
7. Verify that the corrective action has eliminated the problem

Laboratory measurement quality control failures are evaluated by the NWQL and USGS Sediment Laboratory staff. The dispositions of such failures and conveyance to the Research Project Manager and TSSWCB are discussed in Section B4 under "**Deficiencies, Nonconformances and Corrective Actions Related to Chain-of-Custody".**

B6 Equipment Testing, Inspection, and Maintenance Requirements

Manufacturers' recommendations for scheduling testing, inspection, and maintenance of each piece of field equipment will be followed. All laboratory tool, gauge instrument, and equipment testing and maintenance requirements are contained within laboratory standard operating procedures. Records of all tests, inspections, and maintenance are maintained by the USGS laboratories. These records will be available for inspection by the TSSWCB.

Each of the two streamflow stations are to be monitored via the satellite network at least once a week by USGS. Research will assume primary responsibility for ensuring the stations are on line and equipment is functioning.

Each station is to be personally visited at least twice monthly by the Research technician and once monthly by the USGS Project Chief or technician jointly with Research technician. During these visits the following are to be checked:

- Battery/solar panel system
- Clean rain gage
- Sampler pump operation
- Check sample line intake
- Mow area around shelter and other equipment

B7 Instrument/Equipment Calibration and Frequency

Procedures for inspection/calibration of field meters (temperature, specific conductance, and ph) are included in section 8 (Calibration Procedures and Frequency) of the USGS QAPP (Appendix E). Calibration of automatic samplers involves checking that proper sample volumes are retrieved during a pump cycle. The automatic sampler calibration is performed during installation of equipment and after each sample event. The USGS maintains spare meters and automatic samplers so that equipment that does not meet calibration standards can be replaced relatively quickly.

B8 Inspection/Acceptance for Supplies and Consumables

Consumable field supplies include sample bottles, sample preservatives, and sample equipment cleaning chemicals and deionized water. Other material will be obtained directly from laboratory supply vendors. Sample bottles and sample preservatives are obtained from the USGS NWQL. The USGS San Antonio QA officer will be responsible for insuring that supplies are stocked and meet project sampling requirements and quality criteria. Additional information concerning the role of the NWQL for field supply quality assurance is documented in section 3.6.2 in Apendix F (USGS NWQL QMS).

B9 Non-direct Measurements

No non-direct measurements are planned for this study.
Data has been collected from project sites, from June 2006 to September 2007, under a QAPP developed for TSSWCB project 02-13.

The water-quality data associated with the project listed above were collected and analyzed using similar assessment objectives, sampling techniques, laboratory protocols and data validation procedures as the current project.

Data from these previous projects with direct data collected under the current project will be used to evaluate changes in water quality over time. Because these data were collected and analyzed in a manner comparable to the data collected under this project, no limitations will be placed on their use, except where known deviations have occurred.

B10 Data Management

Water-quality data management practices, including field records, electronic data monitor records, laboratory and other analytical data management, data record review, data storage, and records archival are described in section 10.0 of the USGS Quality Assurance Plan (Appendix E).

C1 Assessments and Response Actions

The commitment to use approved equipment and approved methods when obtaining environmental samples and when producing field or laboratory measurements requires periodic verification that the equipment and methods are, in fact, being employed and being employed properly. This verification will be provided through a field and laboratory performance audit performed by the TSSWCB QA officer or contracted entity. Individual field personnel will be observed during the actual field investigation to verify that equipment and procedures are properly applied. Any problems that are discovered in the monitoring procedures that would affect the quality of data collected at the demonstration sites will be addressed by the project participants and followed up with a corrective action. Follow-up observations will occur within three months when discrepancies are noted.

Table C1 Assessments and Response Actions

Assessment Activity	Approximate Schedule	Responsible Party(ies)	Scope	Response Requirements
Status Monitoring Oversight, etc.	Continuous	Research, USGS	Monitoring of the project status and records to ensure requirements are being fulfilled. Monitoring and review of NWQL performance and data quality	Research and USGS will report to TSSWCB PM via quarterly report
Laboratory Inspections	To be scheduled by TSSWCB QAO	Research QM and TSSWCB QAO	Analytical and QC procedures employed at the laboratory and in the field	Research and USGS have 30 days to respond in writing to the TSSWCB QAO to address corrective actions
Monitoring Systems Audit	To be scheduled by TSSWCB QAO	TSSWCB QAO	The assessment will be tailored in accordance with objectives needed to assure compliance with the QAPP. Field sampling, handling and measurement; facility review; and data management as they relate to the project	Research and USGS have 30 days to respond in writing to the TSSWCB QAO to address corrective actions

The Research Project Manager is responsible for implementing and tracking corrective action procedures as a result of audit findings. Records of audit findings and corrective actions are maintained by the Research Project Manager/QA Manager and the TSSWCB QAO.

If audit findings and corrective actions cannot be resolved, then the authority and responsibility for terminating work is specified in the TSSWCB QMP and in agreements or contracts between participating organizations.

Section C2 Reports to Management

Quarterly progress reports will be generated by Research personnel and will note activities conducted in connection with the water quality monitoring program, items or areas identified as potential problems, and any variations or supplements to the QAPP. Corrective action reports that concern field operations will be maintained in an accessible location for reference at Texas AgriLife Research and Extension Center at Corpus Christi. Corrective actions that concern laboratory operations will be managed through the USGS Laboratory Information Management System (LIMS). Corrective action that results in changes or variations from the QAPP will be made known to pertinent project personnel, documented in an update or amendment to the QAPP and distributed to personnel listed in Section A3.

The field sampling and laboratory analyses for the project will be done according to the QAPP. However, if the procedures and guidelines established in this QAPP are not successful, corrective action is required to ensure that conditions adverse to quality data are identified promptly and corrected as soon as possible. Corrective actions include identification of root causes of problems and successful correction of identified problem. Corrective action reports will be filled out to document the problems and the remedial action taken.

The final report will contain a quality assurance section to address accuracy, precision and completeness of the measurement data. The final report will also discuss any problems encountered and solutions made. The final report is the responsibility of the Project Leader and Texas AgriLife Research Project Manager and USGS Project Chief.

D1 Data Review, Validation and Verification

All data obtained from field and laboratory measurements will be reviewed and verified for integrity and continuity, reasonableness, and conformance to project requirements, and then validated against the data quality objectives outlined in Section A7, "Quality Objectives and Criteria for Measurement Data." Only those data that are supported by appropriate QC data and meet the DQOs defined for this project will be considered acceptable for use.

The procedures for verification and validation of data are described in Section D2, below. The Texas AgriLife Research Project Manager and USGS Project Chief are responsible for ensuring that any pertinent field data are properly reviewed, verified, and submitted in the required format for the project database. The NWQL Chief and the USGS Sediment Laboratory Chief are responsible for ensuring that laboratory data are scientifically valid, defensible, of acceptable precision and accuracy, and reviewed for integrity. The data are then submitted to the Texas AgriLife Research Project Manager and USGS Project Chief in the required format for the project database.

D2 Validation and Verification Methods

All field and laboratory data will be reviewed, verified and validated to ensure they conform to project specifications and meet the conditions of end use as described in Section A7. The staff and management of the respective field, laboratory, and data management tasks, as listed in this project, are responsible for the integrity, validation and verification of the data each task generates or handles throughout each process. The field and laboratory tasks ensure the verification of raw data, electronically generated data, and data on chain-of-custody forms and hard copy output from instruments.

The USGS Project Chief will be responsible for maintaining all data collected from field monitoring activities and sample analyses, with copies provided to the Texas AgriLife Research Project Manager for reporting purposes.

The Texas AgriLife Research Project Manager/QA Manager and USGS Project Chief are responsible for validating that the verified data are scientifically valid, defensible, of known precision, accuracy, integrity, meet the data quality objectives of the project, and are reportable to the TSSWCB.

D3 Reconciliation with User Requirements

Representativeness and comparability of data, while unique to each individual collection site, is the responsibility of the Texas AgriLife Research Project Manager. By following the guidelines described in this QAPP, and through careful sampling design, the data collected in this project will be representative of the actual field conditions and comparable to similar applications. Representativeness and comparability of laboratory sample analyses will be the responsibility of the USGS Project Chief and Quality Assurance Officer.

The Texas AgriLife Research Project Manager will review the final data to ensure that it meets the requirements as described in this QAPP. Data that have been reviewed, verified, and validated will be summarized for each site individually, as well as all sites collectively, for their ability to meet the data quality objectives of the project and the informational needs of water quality agency decision-makers. These summaries will be included in the final report.

Appendix A Runoff Sample Analytes, Reporting Limits, Handling, and References

Schedule 2702 - Nutrients

Description: NAWQA, SW, Nutrients (Fil) + Microkjeldahl P & N (Fil & Unfil)
Analyzing Laboratory(s): USGS – National Water Quality Laboratory, Denver, CO.

Analyte	Lab Code	Parameter Code	M	CAS Number	RL	Unit	RL Type	Container
nitrogen, ammonia	1976	608	F	7664-41-7	0.04	mg/L	lrl	FCC
nitrogen, ammonia + organic nitrogen	1985	623	D	17778-88-0	0.10	mg/L	lrl	FCC
nitrogen, ammonia + organic nitrogen	1986	625	D	17778-88-0	0.10	mg/L	lrl	WCA
nitrogen, nitrite	1973	613	F	14797-65-0	0.008	mg/L	lrl	FCC
nitrogen, nitrite + nitrate	1975	631	E		0.060	mg/L	lrl	FCC
phosphorus	2331	666	G	7723-14-0	0.004	mg/L	lrl	FCC
phosphorus, phosphate, ortho	1974	671	H	14265-44-2	0.018	mg/L	lrl	FCC
phosphorus	2333	665	G	7723-14-0	0.004	mg/L	lrl	WCA

Container Requirements

Quantity	Bottle
1.	**125mL** FCC **Description:** 125 mL Brown polyethylene bottle, **Treatment and Preservation**: filter through 0.45-um filter, use filtered sample to rinse containers, Chill and maintain at 4 deg C, ship immediately
1.	**125mL** WCA **Description:** 125 mL Plain (translucent) polyethylene bottle, use unfiltered sample to rinse bottles **Treatment and Preservation**: acidify with 1 mL of 4.5N (4.5 normal) sulfuric acid (H2SO4), chill and maintain at 4 deg C, ship immediately

References

1. **EPA 365.1**
Determination of Phosphorus by Semi-Automated Colorimetry Revision 2.0, Methods for the Determination of Inorganic Substances in Environmental Samples

2. **OFR 93-125**
Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory – Determination of inorganic and organic constituents in water and fluvial sediments; U.S. Geological Survey Open-File Report 93-125, 217p.
Method ID: I-2522-90, I-2540-90, I-2545-90, I-2601-90

3. OFR 00-170
Patton, C.J., and Truitt, E.P., 2000, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory – Determination of ammonium plus organic nitrogen by a Kjeldahl digestion method and an automated photometric finish that includes digest cleanup by gas diffusion: U.S. Geological Survey Open-File Report 00-170, 31p.
Method ID: I2515-91, I-4515-91

Schedule 1198 – Major Ions

Description: Major LL Anions/Cations (Slattery) USGS – National Water Quality Laboratory, Denver, CO.								
Analyte	**Lab Code**	**Parameter Code**	**M**	**CAS Number**	**RL**	**Unit**	**RL Type**	**Container**
calcium	659	915	D	7440-70-2	0.02	mg/L	lrl	FA
chloride	1259	940	I	5473891	0.010	mg/L	mrl	FU
fluoride	1260	950	D	16984-48-8	0.010	mg/L	mrl	FU
inductively coupled plasma (ICP) setup	2002	L2002				unsp	lrl	FA
magnesium	663	925	C	7439-95-4	0.008	mg/L	lrl	FA
pH, laboratory	68	403	A		0.1	pH	mrl	RU
potassium	2774	935	D	2023692	0.010	mg/L	lrl	FA
silica	667	955	D	7631-86-9	0.04	mg/L	lrl	FA
sodium	675	930	C	7440-23-5	0.20	mg/l	lrl	FA
specific conductance, laboratory	69	90095	A		2.6	uS/cm	mrl	RU
sulfate	1263	945	E	14808-79-8	0.010	mg/L	mrl	FU

Container Requirements	
Quantity	**Bottle**
1.	**250mL** FA **Description:** 250 mL Polyethylene bottle, acid-rinsed **Treatment and Preservation**: Filter through 0.45-um filter, use filtered sample to rinse containers and acidify sample with nitric acid (HNO3) to pH < 2
1.	**250mL** FU **Description:** 250 or 500 mL Polyethylene bottle **Treatment and Preservation**: Filter through 0.45-um filter. Use filtered sample to rinse containers
1.	**250mL** RU **Description:** **Treatment and Preservation**: 250 or 500 mL Polyethylene bottle, use unfiltered sample to rinse bottles

References	
1.	OFR 93-125 Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory – Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p. **Method ID**: I-1472-87
2.	**TWRI B5-A1/89** Fishman, M.J., and Friedman, L.C., 1989, Methods for determination of inorganic substances in water and fluvial sediments; U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545p. **Method ID:** I-2058-89, I-2587, I-2781-89
3.	**Std Meth 20th Ed - 3120** American Public Health Association, 1998, Standard methods for the examination of water and wastewater (20th ed.): Washington, D.C., American Public Health Association, American Water Works Association, and Water Environment Federal, p. 3-37 – 3-43 **Method ID**: 3120-ICP

Appendix B Rainfall Sample Analytes, Reporting Limits, Handling, and References

Schedule 1119 – Rainfall Nutrients

Description: S1119 NWQL, Low Level Nuts + P + Microkjeldahl P and N
Analyzing Laboratory(s): USGS – National Water Quality Laboratory, Denver. CO.

Analyte	Lab Code	Parameter Code	M	CAS Number	RL	Unit	RL Type	Container
nitrogen, ammonia	1980	608	H	7664-41-7	0.010	mg/L	lrl	FCC
nitrogen, ammonia + organic nitrogen	1985	623	D	17778-88-0	0.10	mg/L	lrl	FCC
nitrogen, ammonia + organic nitrogen	1986	625	D	17778-88-0	0.10	mg/L	lrl	WCA
nitrogen, nitrite	1977	613	H	14797-65-0	0.002	mg/L	lrl	FCC
nitrogen, nitrite + nitrate	1979	631	G		0.016	mg/L	lrl	FCC
phosphorus	2331	666	G	7723-14-0	0.004	mg/L	lrl	FCC
phosphorus, phosphate, ortho	1978	671	I	14265-44-2	0.006	mg/L	lrl	FCC
phosphorus	2333	665	G	7723-14-0	0.004	mg/L	lrl	WCA

Container Requirements

Quantity	Bottle
1.	125 mL FCC **Description:** 125 mL Brown polyethylene bottle, **Treatment and Preservation**: Filter through 0.45-um filter, use filtered sample to rinse containers, chill and maintain at 4 deg C, ship immediately
1.	125 mL WCA **Description:** 125 mL Plain (translucent) polyethylene bottle, use unfiltered sample to rinse bottles **Treatment and Preservation:** Acidify with 1mL of 4.5N (4.5 normal) sulfuric acid (H2S04), chill and maintain at 4 deg C, ship immediately

References

1. **PA 365.1**
Determination of Phosphorus by Semi-Automated Colorimetry Revision 2.0, Methods for the Determination of Inorganic Substances in Environmental Samples

2. OFR 93-125
Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory – Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.
Method ID: I-2525-89, I-2542-89, I-2546-91, I-2606-89

3. OFR 00-170
Patton, C.J., and Truitt, E.P., 2000, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory – Determination of ammonium plus organic nitrogen by a Kjeldahl digestion method and an automated photometric finish that includes digest cleanup by gas diffusion: U.S. Geological Survey Open-File Report 00-170, 31p. **Method ID:** I-2515-91, I-4515,91

Sample volume requirements:

125 ml of raw (unfiltered) sample is used for the analysis of all total constituents (total organic nitrogen and total phosphorus).

125 ml of filtered sample is used for the dissolved constituents.

A minimum of 0.15” to 0.2” of rain will be required to analyze for the dissolved constituents. About 0.3” to 0.4” of rain will allow for analysis of all the constituents.

Sample handling:

The sample is to be transferred to a clean, 1 liter, amber bottle in the field and labeled. The sample is to be placed on ice in a cooler. In the Texas AgriLife Research lab, the sample will be transferred to 2- 125 ml bottles. One bottle will contain raw sample. One bottle will contain sample that has passed through a 0.45 micron filter.

Appendix C New Reporting Procedures Based on Long-Term Method Detection Levels and Some Considerations for Interpretation of Water Quality Data Provided by USGS, NWQL, USGS Open File Report 99-193

Appendix C

Appendix D Quality Control at the USGS National Water Quality Laboratory USGS Fact Sheet 026-98

Appendix D

Appendix E USGS Texas Quality Assurance Plan for Water-Quality Activities in the Texas District

Appendix E

Appendix F USGS National Water Quality Laboratory Quality Management System

Appendix F

Appendix G Bacteriological Parameters

Appendix G. Bacteriological Parameters

E. coli (31648), *Enterococcus* (31649) and fecal coliform (31616) analyses will follow methods shown in the table below, with the exception of cases where samples are received at a time which precludes preparation of three media. In those cases *E. coli* and *Enterococcus* will be analyzed using IDEXX Colilert (31699) and IDEXX Enterolert (31701) respectively.

PARAMETER	UNITS	MATRIX	METHOD	Parameter Code	AWRL	Lab Reporting Limit (RL)	RECOVERY AT RLs	PRECISION (RPD of LCS/LCS dups)	BIAS %Rec. of LCS	Lab
E. coli	cfu/100 mL	water	SM 9213-D.3	31648	1	1	NA	3.27 Rlog/n*	NA	A&M-CC
E. coli, IDEXX Colilert	MPN/100 mL	water	SM 9223-B	31699	1	1	NA	3.27 Rlog/n*	NA	A&M-CC
Enterococcus	cfu/100 mL	Water	EPA/821R-97/004	31649	1	1	NA	3.27 Rlog/n*	NA	A&M-CC
Enterococcus, IDEXX Enterolert	MPN/100 mL	water	ASTM D-6503	31701	1	1	NA	3.27 Rlog/n*	NA	A&M-CC
Fecal coliform	cfu/100 mL	Water	SM 9222-D	31616	1	1	NA	3.27 Rlog/n*	NA	A&M-CC

*Based on a range statistic as described in Standard Methods, 20th Edition, Section 9020-B, "Quality Assurance/Quality Control Intralaboratory Quality Control Guidelines. This criterion applies to bacteriological duplicates with concentrations >10 MPN/100mL or 10 organisms/100mL.

United States Environmental Protection Agency (USEPA), "Methods for Chemical Analysis of Water and Wastes," Manual #EPA-600-4-79-020
American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF), "Standard Methods for the Examination of Water and Wastewater," 20th Edition, 1998
TCEQ SOP - *Surface Water Quality Monitoring Procedures Volume 1: Physical and Chemical Monitoring Methods for Water, Sediment and Tissue* (December 2003) or subsequent editions.
American Society for Testing and Materials (ASTM) Annual Book of Standards, Vol 11.02

Appendix H   TAMU Environmental Microbiology Laboratory Chain-of-Custody Form

Appendix H.   TAMU Environmental Microbiology Laboratory Chain-of-Custody Form

Texas A&M University-Corpus Christi
The Island University

Chain of Custody Form

Physical and Life Sciences
6300 Ocean Drive
Corpus Christi, Texas 78412

P.I.: Dr. Joanna Mott
Texas A&M University–Corpus Christi
Environmental Microbiology Lab

Project Leader:	Phone:	Fax:	Project Name/Location:	Project No.
	361-825-3262	361-825-3719		

Samplers (sign):

Lab Analysis Request

TAMU-CC

Sampling Identification No:	Lab Only	Total Containers	Media Code	Matrix: Liquid	Matrix: Soil	Preserved (w/ice): $Na_2S_2O_3$ Added Mark "X" on lid	Preserved (w/ice): Ice/Ref (Only)	Sampling: Date	Sampling: Time		Pulse Field Gel Electrophoresis	Fecal Coliforms SM20 9222-D	Escherichia coli SM 20 9213 D	Enterococci EPA 1600	Clostridium perfringens	mHPC SM20 9215-A	Epifluorescence SM20 9216-B	IDEXX® Enterolert™		Remarks

Relinquished by: (Print)	Date:	Time:	Received by: (Print)	Date:	Time:
(Sign)			(Sign)		

2002

Appendix I NELAP-RECOGNIZED LABORATORY ACCREDITATION CERTIFICATE, USGS NWQL LABORATORY

Texas Commission on Environmental Quality

NELAP-Recognized Laboratory Accreditation is hereby awarded to

USGS NATIONAL WATER QUALITY LABORATORY
P.O. BOX 25046 BUILDING 95 MS 407 DENVER FEDERAL CENTER
DENVER , CO 80225-0046

in accordance with Texas Water Code Chapter 5, Subchapter R, Title 30 Texas Administrative Code Chapter 25, and the National Environmental Laboratory Accreditation Program.

The laboratory's scope of accreditation includes the fields of accreditation that accompany this certificate. Continued accreditation depends upon successful ongoing participation in the program. The Texas Commission on Environmental Quality urges customers to verify the laboratory's current accreditation status for particular methods and analyses.

Certificate Number: T104704291-08-TX
Effective Date: 12/5/2007
Expiration Date: 12/31/2008

Executive Director
Texas Commission on Environmental Quality