Clean Water Act §319(h) Nonpoint Source Grant Program

Maintaining Sediment Prevention through the Repair of Floodwater Retarding Structures in McCulloch County

Study Element Tasks: Sedimentation Surveys and Sediment Coring

Texas State Soil and Water Conservation Board
Project 01-21

Quality Assurance Project Plan
Revision 0

prepared by
Baylor University
Department of Geology

Effective Period: Upon USEPA Approval through March 2008

Questions concerning this QAPP should be directed to:

Dr. John A. Dunbar, Associate Professor
Baylor University, Department of Geology
One Bear Place 97354
Waco, TX 76798-7354
john_dunbar@baylor.edu
(254) 710-2191

This page intentionally left blank.

Section A1: Approval Sheet

Maintaining Sediment Prevention through the Repair of Floodwater Retarding Structures in McCulloch County – Study Element Tasks: Sediment Surveys and Sediment Coring

United States Environmental Protection Agency (USEPA), Region VI

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

Signature: Jerry Mercilliott Date: 1/22/08

Name: Ellen Caldwell
Title: Texas NPS Project Officer, Assistance Programs Branch

Signature: Ellen Caldwell Date: 1-22-08

Texas State Soil and Water Conservation Board (TSSWCB)

Name: TJ Helton
Title: NPS Grant Administrator/Project Manager

Signature: TJ Helton Date: 1/14/2008

Name: Aaron Wendt
Title: Quality Assurance Officer

Signature: Aaron Wendt Date: 1/14/2008

Baylor University, Department of Geology (BUDG)

Name: John A. Dunbar, Ph.D.
Title: Associate Professor; Project Coordinator

Signature: John A. Dunbar Date: 12/14/07

Baylor University, CRASR (CRASR)

Name: Jeffery Back
Title: Laboratory Manager

Signature: Jeffrey A Back Date: 12/14/07

Name: Steve Dworkin, Ph.D.
Title: Professor; Project Quality Assurance Officer

Signature: Steve Dworkin Date: 12/14/07

Texas A&M University, GERG (GERG)

Name: Terry Wade
Title: Laboratory Manager

Signature: Terry Z. Wade Date: 1/11/08

Section A2: Table of Contents

List of Figures

List of Tables

List of Acronyms and Abbreviations

ARS	USDA Agricultural Research Service
ASCII	American Standard Code for Information Interchange
ATV	all-terrain vehicle
BUDG	Baylor University, Department of Geology
CAR	corrective action report
CRASR	Baylor University, Center for Reservoir and Aquatic Systems Research
CWA	Clean Water Act
DGPS	differential global positioning system
DQO	data quality objectives
FRS	floodwater retarding structure
GPS	global positioning system
GERG	Texas A&M University Geochemical and Environmental Research Group
GC/ECD	Capillary gas chromatography/electron capture detection
KeV	thousands of electron volts
KHz	thousands of cycles per second
LCS	Laboratory Control Standard
LCSD	Laboratory Control Standard Duplicate
NRCS	USDA Natural Resources Conservation Service
pCi/g	$1x10^{-12}$ Curies (picoCurie) radioactivity per gram
QA	quality assurance
QAM	quality assurance manual
QAO	quality assurance officer
QAPP	quality assurance project plan
QC	quality control
QMP	quality management plan
RMS	root-mean-squared error
RPD	relative percent difference
RTK	Real time kinematic GPS
SDI	Specialty Devices, Inc. of Wylie, Texas
SPLUS	statistical analysis software
SOP	standard operating procedure
SWCD	soil and water conservation district
SWQM	surface water quality monitoring
TCEQ	Texas Commission on Environmental Quality
TSSWCB	Texas State Soil and Water Conservation Board
TWDB	Texas Water Development Board
USLE	Universal Soil Loss Equation
USACE	United States Army Corps of Engineers
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
µCi	$1x10^{-6}$ Curies (microCurie) radioactivity

Section A3: Distribution List

Organizations, and individuals within, which will receive copies of the approved QAPP and any subsequent revisions include:

U.S. Environmental Protection Agency, Region VI
6WQ-AT
1445 Ross Avenue, Suite 1200
Dallas, TX 75202-2733

Name: Ellen Caldwell
Title: Texas NPS Project Manager

Texas State Soil and Water Conservation Board
PO Box 658
Temple, TX 76503

Name: Aaron Wendt
Title: QAO

Name: TJ Helton
Title: Project Manager

Baylor University, Department of Geology
One Bear Place 97354
Waco, TX 76798-7354

Name: John A. Dunbar, Ph.D.
Title: Associate Professor; Project Coordinator

Name: Peter Allen, Ph.D.
Title: Professor, Field and Data Supervisor

Baylor University, Center for Reservoir and Aquatic Systems Research
One Bear Place 97178
Waco, TX 76798-7178

Name: Jeffery Back, Ph.D.
Title: Laboratory Manager, CRASR

Name: Steve Dworkin, Ph.D.
Title: Professor; QAO

Texas A&M University, Geochemical and Environmental Research Group
833 Graham Road
College Station, TX 77845-3149

Name: Terry Wade, Ph.D.
Title: Deputy Director-Environmental Studies

Section A4: Project/Task Organization

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

USEPA Region VI – Dallas, Texas. Provides project oversight and funding at the federal level.

Ellen Caldwell, Texas NPS Project Manager

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 CWA. Reviews and approves the QAPP, project progress, and deliverables.

TSSWCB – Temple, Texas. Provides project oversight and funding at the state level.

TJ Helton, 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.

Aaron Wendt, QAO

Reviews and approves QAPP and any amendments or revisions and ensures distribution of approved/revised QAPP 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 assurance (QA), quality control (QC), and reporting under the CWA §319(h) NPS Grant Program. Monitors implementation of corrective actions. Coordinates or conducts audits of field and laboratory systems and procedures.

BUDG – Waco, Texas. Project Facilitator. Provides the primary point of contact between the TSSWCB and subcontractors. Performs sediment coring and sediment surveys. 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.

Dr. J. A. Dunbar, Associate Professor, Geophysics; Project Coordinator

As Project Coordinator, responsible for ensuring that tasks and other requirements in the contract are executed on time and as defined by the grant workplan; assessing the quality of work by participants; submitting accurate and timely deliverables and costs to the TSSWCB Project Manager; and coordinating attendance at conference calls, meetings, and related project activities. Also responsible for ensuring that the reduction of the sediment survey data and the ^{137}Cs analyses are conducted according the QA/QC requirements and that the required records are kept as described by this QAPP.

Dr. Peter M. Allen, Professor, Hydrology; Data Supervision; Field Supervision

Responsible for coordinating field sampling activities. Responsible for ensuring that scheduled tasks and other requirements in the contract are executed on time and in accordance with the QA/QC requirements 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. Performs validation and verification of data before the report is sent to the TSSWCB.

CRASR – Waco, Texas. Laboratory that will perform sediment digestion, and analyses for nutrients and organic and total carbon.

Dr. Jeffery Back, CRASR Laboratory Manager

Responsible for coordinating laboratory digestion and analysis of sediment samples for organic and total carbon. Responsible for ensuring that these analyses are conducted according the QA/QC requirements and that the required records are kept as described by this QAPP.

Dr. Steve Dworkin, CRASR QAO

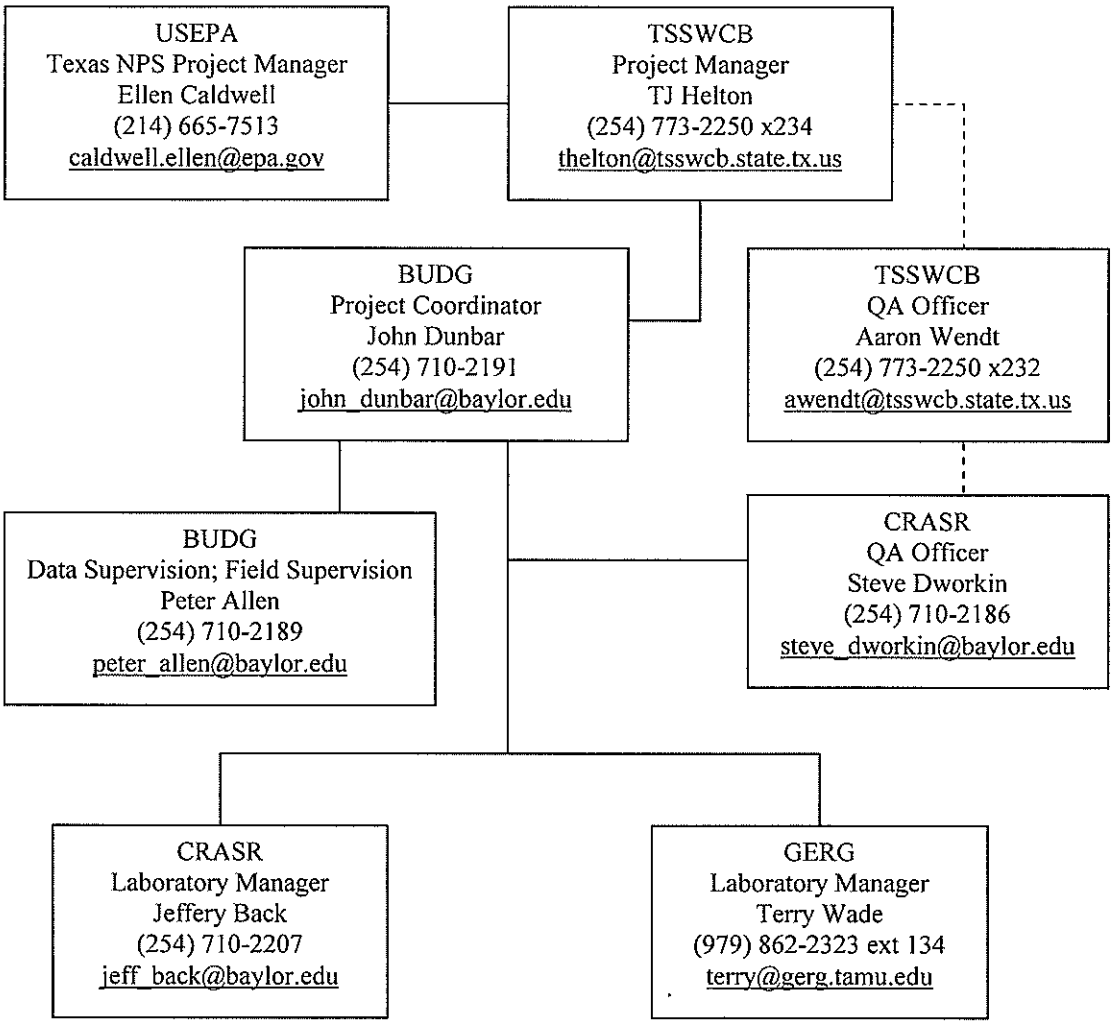
Responsible for determining that the QAPP meets the requirements for planning, QC, QA, and reporting for activities conducted by BUDG. Responsible for maintaining the official, approved QAPP and for distribution to project partners identified in Section A3. Maintains records of QAPP distribution, including appendices and amendments. Coordinates the research and review of technical QA material and data related to sediment coring, sediment surveying and analytical techniques.

GERG – College Station, Texas. Laboratory that will perform analyses for trace metals and pesticides.

Dr. Terry Wade, Laboratory Manager

Responsible for coordinating laboratory analysis of digested sediment extract samples for trace metals and pesticides. Responsible for ensuring that these analyses are conducted according to the QA/QC requirements and that the required records are kept as described by this QAPP.

Figure A4-1. Project Organization Chart



Dashed lines indicate communication only.

Section A5: Problem Definition/Background

The Flood Control Act of 1944 (PL 78-534) and the Watershed Protection and Flood Prevention Act of 1954 (PL-83-566) gave the USDA responsibility in selected watersheds across the United States to reduce runoff, erosion and stream flow. One of the selected watersheds in Texas was the Middle Colorado River watershed. In the 1950s and 1960s, 30 floodwater-retarding structures (FRS) were installed along Brady Creek (BC, 21), Deep Creek (DC, 6), the Lower San Saba River (LSSR, 1), and the Southwest Laterals (SWL, 2) in McCulloch County. All McCulloch County FRS were authorized as PL-534 structures. These structures were some of the first of almost 11,000 such FRS that have been built throughout the United States since the 1950s. FRS have served well in preventing flooding and reducing NPS pollution by trapping sediment and associated adsorbed contaminants from the uplands (cropland and rangeland) of these watersheds. By slowing storm flows, these structures also have a positive impact on channel and bank erosion in streams below the structures. However, after 50 years of benefit, many have reached or are rapidly approaching the end of their serviceable lives. For this reason there is considerable current interest is assessing the status of FRS in terms of where they are in their useful lives and the impact they have had on water quality. To date, most of the recent attention in Texas has been focused on FRS in the more populated central and eastern parts of the state. This study will be the first study since the 1970s that will investigate the status of FRS in McCulloch County.

Table A5-1. Water Quality Impairments and Concerns for Waterbodies of Interest

FRS Watershed	Segment	Impairment	Concerns
Brady Creek	1416A Brady Creek	depressed dissolved oxygen	ortho-phosphorus, total phosphorus, nitrate, chlorophyll-a
Deep Creek and Southwest Laterals	1410 Colorado River below O.H. Ivie Reservoir	-	-
San Saba River	1416 San Saba River	-	bacteria
All 4 watersheds of interest	1408 Lake Buchanan	-	chlorophyll-a

Based on the *2006 Texas Water Quality Inventory and 303(d) List.*

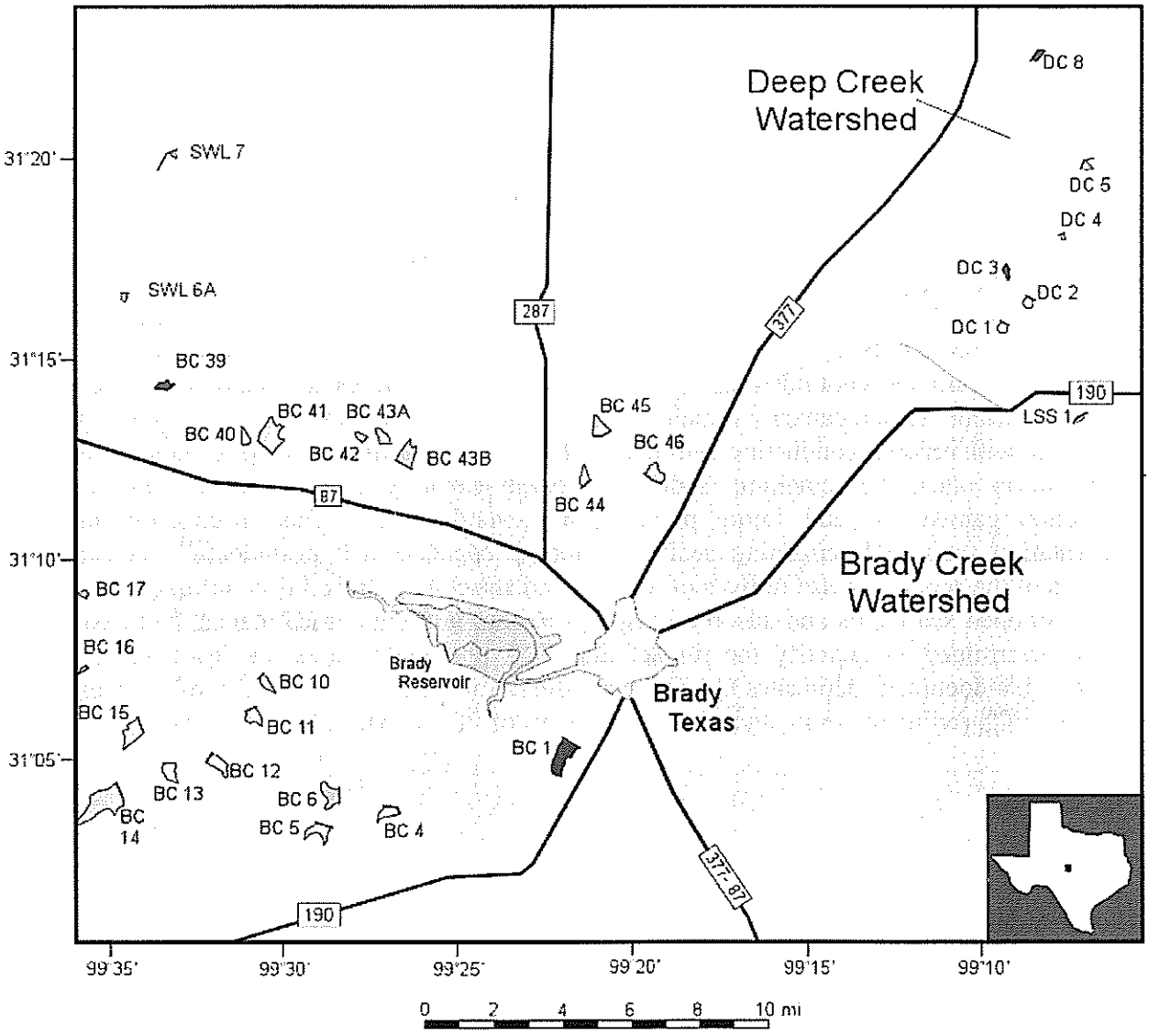
NRCS performed reservoir sediment studies in 1951, 1966, and 1972 on two FRS in McCulloch County, specifically DC 8 and DC 3. The analysis showed that from 1951 to 1972 a total of 188 tons of sediment was deposited in DC 8, equating to an average annual storage loss of 0.92%. The analysis on DC 3 from 1953 to 1971 revealed that a total of 2,903 tons of sediment was deposited resulting in an average annual storage loss of 1.25%. Intensive monitoring by the Texas Institute for Applied Environmental Research (TIAER), in 1993 in the North Bosque River watershed, showed that FRS directly reduce NPS sediment loading, excessive nutrients, bacteria, and pesticides.

As critical components of FRS in McCulloch County deteriorate and the hazard of dam failure increases, the local owners have only two economically viable remediation options. One option would be to simply breach the dams. This would remove the hazard of dam failure, but could

potentially result in adverse environmental impacts in downstream floodplains, ecosystems, and water supply reservoirs. In addition to forgoing continued flood protection and trapping of sediment and contaminants, the sediment and contaminants trapped by the reservoirs in the preceding 50 years would be subject to remobilization and movement downstream. Brady Creek Reservoir, which is the primary drinking water supply for the City of Brady and surrounding communities and a FRS itself, is located downstream of numerous FRS in McCulloch County. If the upstream FRS were removed, a significant rainfall within a short time span could potentially devastate the Brady Creek Reservoir, depriving approximately 5,000 people of a reliable water supply. This situation is currently being faced by water districts throughout the state.

The goal of this project is to implement a second, more environmentally sound, remediation option for the FRS in McCulloch County. This will involve the repair of failing critical components, particularly the outlet works, restoring them to safe operating condition. The repairs will permit the continued safe operation of these structures for many years, provided there is sufficient storage capacity remaining for future sedimentation. Hence, a second part of the project will involve conducting sediment surveys of selected reservoirs to determine past sedimentation rates, the remaining sediment storage capacity, and sediment quality. The information gained will aid future planning in several ways. The information on past sedimentation rates and remaining sediment storage capacity will provide well constrained estimates of the remaining useful lives of the repaired structures. In addition, information on the mass of trapped sediments and adsorbed organic carbon, nutrients, trace metals, and pesticides will be determined to quantify the impact that FRS potentially have on downstream water quality. This document delineates QA/QC procedures for Tasks 3, 4, 5, and 6 of the workplan associated with sediment coring and sediment surveys of FRS in McCulloch County.

Figure A5-1. Project Location Map



The portion of the Brady Creek watershed within McCulloch County is shown in green. The portion of the Deep Creek watershed within McCulloch County is shown in blue. FRS selected for surveying are colored red. FRS selected as backup, in case the primary selections cannot be surveyed within standards, are colored yellow.

Section A6: Project/Task Description

A6.1 Project Task 4: Floodwater-Retarding Reservoir Watershed Analysis

In the early days of the USDA NRCS FRS program, it was standard practice to monitor the volume loss due to sediment in FRS by repeating sediment surveys every 5 to 10 years (Dendy, 1968). However, even in the early days there were so many FRS it was impractical to survey them all. Instead, it was customary to select one or two representative FRS to survey in each major basin and the overall status of FRS with the basin was judged based on the results for these representative structures.

The amount of sediment trapped in a FRS per unit land surface area of its watershed, from a given storm event, depends on factors related to the both the event itself and the properties of the watershed and FRS. Experience has shown that over a 5 to 10 year period differences in event-related factors, such as the intensity and duration of the rainfall, the extent of vegetation, and soil moisture at the time of the event, tend to average out over a given basin (Dendy, 1974). Over the long term the factors that remain are the soil erodability, slope, land use, watershed size, and reservoir trap efficiency. Watershed size is a factor in the amount of sediment trapped per unit area, because not all the sediment eroded from the landscape makes it all the way to the FRS. Small watersheds are more efficient at delivering sediment downstream than large watersheds (Greiner, 1982). The trap efficiency of a FRS in a given storm event is a function of the ratio of the floodwater storage capacity of the structure and the volume of the runoff. Over the long term and within a given basin, FRS trap efficiency is a function of the ratio of the floodwater storage capacity and the watershed area (Dendy, 1974). Hence, the extent to which sedimentation in a FRS per unit area of its watershed is representative of the other FRS within the same basin depends on five main factors. These factors are: (1) soil type, (2) slope, (3) land use, (4) the area of the watershed, and (5) the ratio of the floodwater capacity of the FRS to the watershed area. Table B1-1 gives these properties for the FRS in McCulloch County.

In addition to these physical factors, there are programmatic/historical factors that must be considered in the final FRS selection. First, although all of the FRS in McCulloch County were inspected, only some of the structures required repairs. The preference is to study FRS that were repaired to establish directly the remaining operational life of these structures. In Table B1-1, the 12 FRS that were repaired as a part of this project are indicated by yellow shading. It is preferable to select the oldest FRS to survey, because they provide the longest record of sedimentation and can be dated using the ^{137}Cs method. Hence, FRS that were impounded from 1952 to 1956 are preferred, because the onset of sedimentation coincided roughly with the onset of ^{137}Cs deposition in 1954 ±2 yr. Finally, the preference is to re-survey FRS in the region that were previously surveyed by NRCS. This provides comparability between the new surveys and past surveys and it makes possible the assessment of the change in sedimentation rates over time.

Given these considerations, FRS DC 3 and DC 8 were selected for surveying, because these reservoirs were surveyed by the NRCS in 1951, 1966 and 1972 and the historical comparison with the present conditions will be useful. At the rate of volume loss due to sedimentation

reported for the period between 1953 and 1972, the normal pool volumes of these structures should currently be two-thirds full of sediment. The extent to which the early projected sedimentation rate agrees with the actual long-term sediment rate will be an important result of the study.

The remaining task was to select two more FRS from the structures that were repaired (BC 1, 4, 10, 14, 39, 40, 41, 45 and 46; and DC 1 and 2). The goal was to select the remaining two FRS, such that the average properties of the four selected were as close as possible to the average properties of the 29 FRS within McCulloch County. The primary tools used in this selection process were the USACE National Inventory of Dams (http://crunch.tec.army.mil/nidpublic/webpages/nid.cfm), the Soil Survey of McCulloch County (SCS, 1974), the USDA NRCS Web Soil Survey (http://websoilsurvey.nrcs.usda.gov/app/WebSoilSurvey.aspx), and the Soil and Water Assessment Tool (SWAT) (Neitsch et al., 1005). The details of the selection process using these tools are described in Section B1.

A6.2 Project Task 5: Sediment coring

A6.2.1 Sediment core sampling

Sediment core samples will be collected from the four FRS to be surveyed in McCulloch County. Sediment texture and degree of compaction tend to vary along the axis of reservoirs, with the sediment in backwater regions being coarser and more compacted than that in the deeper regions near the dam (Dendy, 1982). Following the strategy described by Van Metre et al. (2003), three core sites will be selected in each FRS reservoir surveyed to sample sediment variability. One site will be in the deepest water near the dam, one site will be in an intermediate position along the axis of the reservoir and one site will be in the backwater region. Two cores will be collected at each site. One core will be cut open lengthwise to view the stratigraphy intact, for visual inspection and interpretation. The second core will be extruded in 5 cm sub-samples for chemical analysis. The cores will be used for validating acoustical sediment thickness measurements, determining the dry bulk density of the sediment, to provide samples for ^{137}Cs age dating, and to provide samples for determining concentrations of adsorbed contaminants.

Where there is sufficient water depth to float the survey boat, sediment cores will be collected using a submersible vibracoring system. Vibracoring is a standard method for obtaining cores of unconsolidated sediment with little or no compaction of the sample (Lanesky et al., 1979; Smith, 1984). For FRS, with access limited to small boats, the lightweight of the vibracoring equipment makes it the only practical option for collecting cores that penetrate the entire sediment column and into the pre-impoundment material. The BUDG vibracoring system is sufficiently lightweight (50 kg) that it can be deployed from a 14 ft Jon boat fitted with an A-frame and hand-operated winch. The device runs on 24-volt DC current supplied by two 12-volt trolling motor batteries connected in series. The vibrator is connected to the top of an aluminum or stainless steel core tube, with 1.5 mm wall thickness and 76 mm diameter. The vibration causes the sediment to liquefy in a region a few millimeters thick near the core tube wall, allowing the tube to slide into the sediment with little drag. With this device BUDG routinely collect cores up

to 3 m in length that penetrate the entire sediment column and into the pre-impoundment surface in FRS.

To the extent possible, cores will be collected in the water-covered parts of the reservoir. Nutrients and other contaminants in exposed and dried sediment are subject to vertical migration with meteoric water and uptake by plants. Hence, sediments in the parts of reservoirs that are dry most of the year are not the best recorders of trapped contaminants. Where necessary, coring the exposed reservoir bottom will require a different approach. A vibracoring system based on a pneumatic fencepost driver will be used for coring on dry land. Because the sediments are dry and compacted, more power is required to drive the core tube into the sediment. The pneumatic driver essentially hammers the tube into the ground. The land coring system consists of a gasoline-powered air compressor, driver head, and a trailer-mounted tripod with a hand winch for extracting the tube. The system is trailered to the coring site behind a pickup truck. For consistency, the same thin-walled aluminum or stainless steel core tubes will be used for both water and land coring operations. Details of the coring methods to be used in the water and on dry land are described in Sections B2.1.1 and B2.1.2, respectively.

A6.2.2 Physical and chemical analysis

The two cores collected at each site will be used for different analyses. Cores collected in aluminum core tubes, will be cut lengthwise for visual inspection to identify the depth to the pre-impoundment surface base on stratigraphic and sedimentological properties of the core. After visual inspection and interpretation, these cores will be sub-sampled in 5 cm increments for water content analysis and for ^{137}Cs analysis. Half of each 5 cm sub-sample will be dried and stored separately. The remaining portions of the sub-samples will be mixed and then dried to form a single composite sample for the entire core.

BUDG will use the ^{137}Cs method to identify the 1954 and 1964 time lines in one core from each reservoir surveyed. ^{137}Cs is primarily carried by the clay texture fraction within sediment samples. Hence, the core that appears to contain the most complete record of fine-grained sediment will be selected for dating. This will normally be the core from the deepest part of the reservoir. The ^{137}Cs technique is a standard method for identifying age lines in sediment cores that correspond to changes in fallout rates of atmospheric ^{137}Cs in the last 50 years (Van Metre et al. 2003; 2004). Of the FRS in McCulloch County, 6 were impounded in the early-1950s, 7 in the mid-1950s, 11 in the late-1950s, 4 in the early 1960s, and 2 in the 1980s. So, the majority of FRS in McCulloch County were impounded in the mid- to late-1950s. The date of impoundment was an additional criterion used to select the reservoirs to be surveyed, as described in Section B1. To the extent possible, reservoirs impounded in the early to mid-1950s were chosen. The older reservoirs are favored for several reasons. They provide a longer record of sedimentation. The presence of detectable concentrations of ^{137}Cs in sub-samples of the cores will indicate post-impoundment deposition, and identification of the 1964 peak in ^{137}Cs in the cores will make it possible to compare sedimentation rates from impoundment to 1964 and from 1964 to present.

A6.2.3 Chemical analysis

The core samples will also be used to establish the quality of the sediment sequestered in the FRS in McCulloch County. Sediment quality is of interest for two reasons. First, it is a measure of the amount of contamination that has been removed from surface water over the life of the FRS and thereby was not transported into downstream waterbodies, including major water supply reservoirs. Second, it is a measure of how much contamination could potentially be remobilized and added to surface water, if the FRS were removed. Average concentrations of contaminants within the post-impoundment sediment will be determined by forming a composite sample from the core sub-samples. The composite samples will be analyzed to determine concentrations of total organic carbon, common nutrients (total nitrogen, total phosphorus, NH_3-N, NO_2-N, and NO_3-N), a suite of trace metals, and a suite of common pesticides. The carbon and nutrient analyses will be performed at the Baylor University CRASR Laboratory. The trace metal and pesticide analysis will be performed at the Texas A&M University GERG Laboratory. These analyses will determine the mass of each contaminant species per gram of dry sediment sample. These values will be used to estimate the total mass of each contaminant species trapped within the reservoirs that would have potentially remained in the surface water, if the reservoirs were not present. Details of the analysis method used in each case are given in Section B4.1.3.

A6.3 Project Task 6: Sediment surveys

The initial storage capacity of water reservoirs is divided into allotments for water supply or conservation storage, floodwater storage, and sediment storage. The useful life of reservoirs is limited by the capacity of the sediment storage pool and the sedimentation rate. FRS differ from conventional water supply reservoirs in that a much higher percentage of the total capacity is allotted to floodwater storage. This pool is kept empty, except during major runoff events, as a result of the placement of the principle outlet works at a relatively low elevation. The conservation pool is small and doubles as the sediment pool. Once the conservation pool is filled with sediment, the normal outlet works do not work properly without continuous maintenance and the dam becomes a hazard.

To address this hazard, in the early days of the FRS program it was standard practice to monitor the loss of volume in representative FRS by repeating bathymetric surveys every five to ten years. In these early days, water depth was measured manually with sounding lines and sediment thickness was measured by manually penetrating the sediment with spud bars. Navigation was accomplished by following cables stretched across small reservoirs or by shore-based range-angle observations for larger reservoirs. In the 1960s, paper-recording acoustic fathometers replaced the sounding lines used to determine water depth. These surveys required weeks of fieldwork and months of data analysis to produce estimates of the remaining reservoir volume and the volume of trapped sediments.

Due to budget cut backs, the practice of routinely surveying FRS was eventually dropped and, like the FRS in McCulloch Country, most FRS throughout the United States have not been surveyed since the mid 1970s. Since that time, reservoir surveying technology has changed.

Sediment surveys of large water supply reservoirs are now conducted using digital-recording acoustic fathometers and DGPS positioning (USACE, 2001). DGPS systems used in reservoir surveys receive real-time correction signals from satellites or fixed U.S. Coast Guard ground stations and have sub-meter horizontal accuracy. The data collected in reservoir surveys are used to map the bathymetry of the reservoir and compute the water storage capacity at the design pool elevation. The volume of post-impoundment sediment that has been trapped in the reservoir is inferred indirectly from the change in water capacity between the time of impoundment or a previous survey and the new survey. The new data collection and analysis technology has reduced the labor involved in sediment surveys by more than a factor of ten.

Surveys of FRS present special logistical problems. FRS are normally not equipped with boat ramps, which limits the size of survey vessels that can be used to small boats that can be trailered off-road or carried to the water's edge and deployed from the shore. Conventional equipment used in modern reservoir sediment surveys is too bulky and heavy to be deployed on vessels small enough to be used in FRS. In addition, FRS are normally not filled to capacity and portions of the reservoir bottom that are underwater when the reservoir is filled to capacity, are dry most of the time. For these reasons, special equipment and methods are required to conduct modern-style sediment surveys in FRS. From 2002 to 2005, BUDG conducted a USDA-funded project to develop and implement new surveying technology specifically for FRS. In the water covered portions of FRS, the survey method involves the use of a special shallow-water boat, a light-weight, five-frequency sub-bottom acoustic profiling system, and a light-weight underwater vibracoring system. For dry land portions of FRS, ATV-mounted, real-time kinematic GPS (RTK) and pneumatic vibracoring systems are used. To date BUDG has surveyed 23 FRS in Texas, Oklahoma, Arkansas and Wisconsin. The sub-bottom profiler and vibracore systems are commercially available from Specialty Devices, Inc. of Wylie, Texas. Various Federal and State agencies have purchased copies of these components, particularly the USGS, USACE, and TWDB. BUDG will use these methods to survey and core the four FRS in this project. The details of the complete method are described in Section B4.2.

Table A6-1. Project Plan Milestones

Milestone	Description	Date
3.1	Final QAPP for sediment surveys and coring	Nov. 1, 2007
4.2	Select representative FRS for surveying	Jan. 1, 2007
5.1	Complete sediment core sample collection	Jan. 1, 2008
6.1	Complete surveys of FRS	Jan. 1, 2008
5.2	Physical and ^{137}Cs analysis complete	Feb. 1, 2008
6.2	Analysis of water and sediment storage volumes complete	March 1, 2008
6.3	Completion of final report	March 31, 2008

Section A7: Quality Objectives and Criteria

The project objective is to generate data that can be used to determine the status of FRS in McCulloch County and to contribute to the understanding of the performance of such structures throughout Texas. Specifically, the objective is to quantify sediment deposition volumes and mass and to quantify the mass of adsorbed contaminants in the trapped sediment. To do this, data will be collected that complies with USACE and USDA procedures for conducting reservoir sediment surveys and EPA methods and practices for SWQM programs. The measurement performance specifications to support the project objectives are specified in Tables A7-1 and A7-2.

The overall data quality objective for this project is to develop and implement procedures that will ensure the collection of representative data of known, acceptable, and defensible quality. Parameters used to assess data quality include precision, accuracy, bias, representativeness, comparability, and completeness.

Table A7-1. Physical Measurement Performance Specifications

Parameter	Units	Name of Method or Instrument	Method Reference	Accuracy
Water Temperature	°C	YSI Meter	Appendix A	± 1 °C
Water Conductivity	µS/cm	YSI Meter	Appendix A	± 5%
Sediment Water Content by Mass	kg/kg	ASTM D2216-92	ASTM D2216-92	± 5%
Dry Bulk Density	kg/m^3	ASTM D2216-92	ASTM D2216-92	± 5%
^{137}Cs Activity	pCi/g	Gamma Ray Spectrometry	Bennett et al. (2005)	± 10%
Water Depth	m	Acoustic fathometry	Dunbar et al. (1999; 2001)	± 10 cm
Sediment Thickness	m	Acoustic Sub-bottom Profiling	Dunbar et al. (1999; 2001)	± 20 cm
Horizontal Position	m	DGPS	USACE (2001)	± 1 m
Land Surface Elevation	m	RTK GPS	USACE (2001)	± 3 cm

Table A7-2. Chemical Measurement Performance Specifications

PARAMETER	UNITS	METHOD	DESCRIPTION	Lab Reporting Limits	Recovery at Reporting Limits	PRECISION (RPD of LCS/LCSD)	BIAS (% Rec. LCS/LCSD mean)
Total Organic Carbon	mg/L	EPA 415.1	Appendix B	2.0 (AWRL)	75-125	80-120	80-120
Total Nitrogen	mg/L	EPA 353.2	Appendix C	0.01	75-125	80-120	80-120
Total Phosphorus	mg/L	EPA 365.3	Appendix D	0.01	75-125	80-120	80-120
NH_3-N	mg/L	EPA 350.1	Appendix E	0.02	75-125	80-120	80-120
NO_2-N+NO_3-N	mg/L	EPA 350.1	Appendix E	0.02	75-125	80-120	80-120
Aluminum	mg/L	EPA 1620	Appendices G, H	0.2	75-125	80-120	80-120
Arsenic	mg/L	EPA 1620	Appendices G, H	0.5	75-125	80-120	80-120
Barium	mg/L	EPA 1620	Appendices G, H	0.2	75-125	80-120	80-120
Cadmium	mg/L	EPA 1620	Appendices G, H	0.005	75-125	80-120	80-120
Chromium	mg/L	EPA 1620	Appendices G, H	0.01	75-125	80-120	80-120
Copper	mg/L	EPA 1620	Appendices G, H	0.025	75-125	80-120	80-120
Iron	mg/L	EPA 1620	Appendices G, H	0.1	75-125	80-120	80-120
Lead	mg/L	EPA 1620	Appendices G, H	0.005	75-125	80-120	80-120
Magnesium	mg/L	EPA 1620	Appendices G, H	5	75-125	80-120	80-120
Manganese	mg/L	EPA 1620	Appendices G, H	0.015	75-125	80-120	80-120
Mercury	mg/L	EPA 1620	Appendices G, H	0.0002	75-125	80-120	80-120
Vanadium	mg/L	EPA 1620	Appendices G, H	0.05	75-125	80-120	80-120
Zinc	mg/L	EPA 1620	Appendices G, H	0.02	75-125	80-120	80-120
Aldrin	ng/g	EPA 612	Appendices I, J	0.5	75-125	80-120	80-120
Alpha-Chlordane	ng/g	EPA 612	Appendices I, J	0.5	75-125	80-120	80-120
Dieldrin	ng/g	EPA 612	Appendices I, J	0.5	75-125	80-120	80-120
Endrin	ng/g	EPA 612	Appendices I, J	0.5	75-125	80-120	80-120
Heptachlor	ng/g	EPA 612	Appendices I, J	0.5	75-125	80-120	80-120
Heptachlor Epoxide	ng/g	EPA 612	Appendices I, J	0.5	75-125	80-120	80-120

PARAMETER	UNITS	METHOD	DESCRIPTION	Lab Reporting Limits	Recovery at Reporting Limits	PRECISION (RPD of LCS/LCSD)	BIAS (% Rec. LCS/LCSD mean)
Hexachlorobenzene	ng/g	EPA 612	Appendices I, J	0.5	75-125	80-120	80-120
Lindane	ng/g	EPA 612	Appendices I, J	0.5	75-125	80-120	80-120
Mirex	ng/g	EPA 612	Appendices I, J	0.5	75-125	80-120	80-120
Trans-Nonachlor	ng/g	EPA 612	Appendices I, J	0.5	75-125	80-120	80-120
o-p' DDT	ng/g	EPA 612	Appendices I, J	0.5	75-125	80-120	80-120
p-p' DDT	ng/g	EPA 612	Appendices I, J	0.5	75-125	80-120	80-120

References for Table A7-2:

1. USEPA, *Methods for Chemical Analysis of Water and Wastes*, EPA-600-4-79-020.
2. American Public Health Association, American Water Works Association, and Water Environment Federation, *Standard Methods for the Examination of Water and Wastewater*, 21st Edition, 2005.
3. TCEQ, *SWQM Procedures Volume 1: Physical and Chemical Monitoring Methods for Water, Sediment and Tissue* (December 2003).
4. American Society for Testing and Materials (ASTM) Annual Book of Standards, Vol. 11.02.

A7.1 Accuracy

Accuracy is a measure of the absolute difference between a measurement of a quantity and the known value of that quantity. Accuracy is the most stringent measure of data quality. In laboratory chemical analyses, accuracy is determined by comparing measured values produced by analysis following specified SOPs and the known values of standard samples. Standard samples are prepared to specified levels of accuracy by an independent laboratory using accepted methods and instrumentation, are identified by manufacturer and lot number, and are traceable. In bathymetric surveys, the accuracy of acoustical water depth measurements is determined by comparing water depth measurements to an artificial acoustic target lowered to an independently known depth below the acoustic transducer. The accuracy of acoustical measurements of the thickness of post-impoundment sediment is determined by comparison between acoustic measurement at a point and co-located coring results. The accuracy of GPS position measurements is determined by comparison positions produced by the GPS system and the known location of an independently established benchmark near the survey area.

A7.2 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. Precision results are plotted on quality control charts that are based on historical data and used during evaluation of analytical performance. Performance specifications for LCS/LCSD are defined in Table A7.2.

Sample splits are used to assess the variability of sample handling, preservation, and storage, as well as the analytical process. For water samples, sample splits are commonly made in the field. However, for core samples of unconsolidated sediments, opening the core in the field exposes the sediment to oxygen and transporting unconfined wet sediment in sample bags causes the pore water and sediment to separate. The physical and chemical properties of the samples are best preserved by sealing the cores in the field and maintaining the cores at a temperature of 4 °C until the cores are sub-sampled and the sub-samples can be prepared for analysis (EPA, 2001). For this reason, in this study the core samples will be sealed in the field, placed in ice and transported back to BUDG for sub-sampling. Sample splits will be prepared by splitting the core samples in the laboratory when the cores are first opened. Control limits for laboratory splits are defined in Section B5.

The precision of the acoustic measurements will be determined by collecting multiple extra acoustic profiles that trend parallel to the reservoir thalweg and cross the normal survey profiles at approximately right angles. During post-processing these profiles will be independently interpreted in the same way as the regular survey profiles. A feature of the interpretation software, *Depthpic*, will be used to find all the intersections between crossing lines and to compute the RMS difference between the water depth and sediment thickness measurements at

the intersection points. The resulting values are measures of the precision of the water depth and sediment thickness measurements. If all sub-systems of the survey system are working properly, including acoustics, navigation, and human interpretation, then the measurements should be the same at locations the navigation system determines are the same points on the reservoir. RMS errors in excess of 10 cm in water depth and 20 cm in sediment thickness will indicate a problem has occurred in some part of the survey system. In addition, the precision of the navigation system will be tested manually at least twice during each field day. This test will be performed by recording the position of a fixed point on shore at the site in the morning prior to beginning the survey. The position will then be reoccupied and measured at midday and at the end of the field day. If the three positions do not agree to within 1 m, the navigation system will be judged faulty, which would invalidate the data collected since the last successful test.

The DGPS navigation system is a critical part of the acoustic profiling, land surveying and coring operations. If the navigation system is not working properly, no useful data can be collected. For this reason, the Hypack software used to control the navigation continuously monitors the number and quality of the signals received from the GPS satellites and the correction signal from the ground reference station. During operations, if the quality of these signals drops to the point that the instrument is receiving signals from fewer than the required number of satellites or the correction signal is lost, so that position accuracy of 1 m cannot be maintained, the unit flashes a warning on the computer monitor and operations will be stopped until the problem is corrected. In most cases, problems can be corrected by relocating the antennas. In cases in which overhead obstructions, such as tree canopy, is obstructing the signal, nothing can be done. In these cases, the obstructed portions of the site cannot be surveyed. Project control limits for hydrographic surveying and physical analysis of sediments are specified in Table A7.1.

A7.3 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 LCS/LCSD are specified in Table A7.2.

For acoustic profiling, the target horizontal accuracy is 1 m root-mean-square (RMS) error and target vertical accuracy is 10 cm RMS error. These accuracy levels meet the minimum performance standards for soft bottom material navigation and dredging support surveys in the USACE hydrographic surveying engineering manual (USACE, 2001), and further described in Section B2 (Positioning). Accuracy will be demonstrated in the cross-check analysis, which provides a confidence level for each sonar frequency.

A7.4 Representativeness

The data collected are required to be representative of the target population to be studied. The representativeness of the data depends on 1) the sampling locations, 2) the number of samples collected, 3) the variability of the population being sampled, and 4) the sampling procedures. Site selection and sampling of pertinent media (i.e., sediment) and use of only approved analytical methods will assure that the measurement data represent the population being studied at the site. At the largest scale, 4 of the 30 FRS structures in McCulloch County will be selected for surveying, based on soils, land use, and topography to be representative of all the structures. Then within a given reservoir, sediment core locations will be selected to be representative of the overall sediment properties, by sampling sediment deposited in the different flow regimes in the reservoirs (backwater, mid-lake, and deep water). The goal for meeting total representation of the sediment within the surveyed reservoirs will be tempered by the funding available and the project duration.

A7.5 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.

Differences in data collection methodologies between earlier NRCS volumetric surveys, done in the 1950s to 1970s, prior to the advent of DGPS positioning, and the multi-frequency hydrographic survey with DGPS navigation done in this study may result in limitations in data comparability. In addition, 35 years of deposition and erosion have occurred since the most recent NRCS survey in the watershed. Hence, the current and past surveys are expected to differ in terms of the remaining water storage capacity and the amount of trapped sediment in each reservoir. However, the differences between past and current surveys will provide important information about changes in sedimentation rates over time.

To insure comparability with future surveys, the raw survey data will be recorded and archived in UTM meters, using the WGS 1984, NAVD 88, reference system. To facilitate comparisons with past surveys, the current survey results will also be displayed and archived in Texas State Plane Zone 3, Texas-Central, FIPS 4203, Feet, horizontal coordinate system and the NAD 1929 vertical datum system. All results will be computed and reported in the appropriate metric units (e.g., hectares, cubic meters, metric tons), and for comparability, the results will also be reported in the appropriate English units (e.g. acres, acre-ft, and tons).

A7.6 Completeness

The completeness of the data is the 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 that 90% data completeness is achieved.

Examples of failures in achieving complete sampling and/or deviations from sample design requirements include the inability to collect sufficient acoustic profiles during sediment surveys. Failures to collect pre-planned acoustic profiles occur as a result of physical obstructions in the water and on land, such as shallow water, trees, stumps, brush, and thick vegetation that prevents access by the survey vessel or ATV on land. The first line of defense against this problem is a pre-survey visit to each candidate reservoir. If more than 10% of the reservoir normal pool area is not accessible by boat or ATV, the backup reservoir will be surveyed, as described in Section B1.

Failures to collect complete cores samples can result from cored material being lost out of the bottom of the core tube or cored material being forced out of the top of the core tube. In these cases, the normal remedy is to collect another core in the same location. In unforeseen cases in which this cannot be done, it is the responsibility of the Field Supervisor to ensure that the actions and resolutions to the problem are documented and that records are maintained in accordance with this QAPP. The Field Supervisor, in consultation with the CRASR QAO and the TSSWCB QAO, will determine if the deviation from the QAPP compromises the validity of the resulting data. Resolution of the situation will be reported to the TSSWCB in the next quarterly report.

Section A8: Special Training/Certifications

There are no requirements for additional staff training or certification for this project. The field personnel and laboratory analysts for this project have a combination of experience, education, and training to demonstrate sufficient knowledge of their function. Experience, education and training are retained in the respective personnel files and can be made available during a technical systems audit. John Dunbar and Peter Allen will conduct the sediment survey and coring operations, including the ^{137}Cs analysis. Together they have conducted acoustic profiling and coring operations in 12 water supply reservoirs and 23 FRS over the last 10 years. The chemical analysis of the core samples will be performed by analysts that work full time at the CRASR and GERG laboratories.

Section A9: Documentation and Records

Hard copies of all field notebooks will be archived by BUDG for at least five years. Electronic copies and/or hard copies of all general maintenance and calibration records for laboratory equipment, laboratory data entry sheets, core sub-sampling forms (Appendix M), calibration logs, COC records (Appendix N) and CARs (Appendix K) will be archived by the BUDG Laboratory for at least five years. In addition, BUDG will archive electronic forms of all project data, including raw acoustic recordings, for at least five years. All electronic files and data will be written onto recordable DVDs for each survey.

Quarterly progress reports will be generated by BUDG and will note activities conducted in planning, conducting surveys and analysis of the resulting data, items identified as potential problems, and any variations or supplements to the QAPP. Variations and amendments to the QAPP must be pre-approved by TSSWCB. CARs that result in 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 the CRASR QAO. The CRASR QAO is responsible for maintaining the official, approved QAPP.

Section B1: Sampling Process Design

B1.1 Design of watershed analysis and process of FRS selection for Project Task 4

As part of this project, a small number (4) of the FRS in McCulloch County will be surveyed and cored. In Project Task 4, the reservoirs to be surveyed were selected on the basis of the factors that most directly influence the long-term rate of sediment accumulation within FRS. Following past sediment yield studies (Greiner, 1982) and the sedimentation yield terms within SWAT (Neitsch et al., 2005) four factors associated with the contributing watershed were considered. These factors were the soil erodability as expressed in the Universal Soil Loss Equation (USLE) K factor, the relief ratio of the watershed (maximum elevation difference divide by the watershed axial length), the primary land use or vegetation within the watershed, and the watershed area. These factors were taken from the SWAT data base. In addition, one characteristic of the FRS structure was considered, the ratio of the floodwater storage capacity and the watershed area, which was computed from data in the USACE National Inventory of Dams (NID). Within a given climate regime, this factor correlates to reservoir trap efficiency (Dendy, 1974). These factors, along with the geographic location of the dam and the date of impoundment for the 30 FRS in McCulloch Country are given in Table B1-1. The approach used for Task 4 was to choose 4 FRS, such that average of these factors is as close to the averages for the 30 FRS in McCulloch County as a whole.

In addition to these physical characteristics, three programmatic/historical factors were considered in the selection process. A preference was given to those FRS that were repaired as part of this project over the others that did not require immediate maintenance. In this way, for the FRS surveyed, a direct measure of the remaining sediment storage capacity and the expected remaining useful life of FRS will be produced. Twelve FRS were repaired in the project, specifically BC 1, 4, 10, 14, 39, 40, 41, 45 and 46, and DC 1, 2, and 3. These FRS are marked by yellow shading in Table B1-1. The age of the FRS will also be considered, in that the older FRS will contain the longest sedimentation record and will benefit the most from ^{137}Cs dating. For these reasons FRS impounded in the early to middle 1950s are favored over FRS impounded later. Then as a final factor considered, FRS that have had prior surveys by the NRCS were favored over those that have not been surveyed, for comparability and to constrain changes in sedimentation over time.

Taking all these factors in consideration, the four primary choices were DC 3 and 8 and BC 1 and 39. The two backup FRS were DC 1 and BC 4. The two Deep Creek sites were chosen, because they had prior surveys and because they are among the oldest FRS in the country. The Two Brady Creek sites were selected, because they are the oldest of the non-Deep Creek sites and in combination with the first two choices, the averages of the physical selection factors of the 4 is near that of the 30 FRS as a whole (Table B1-2). The backup selections are summarized in Table B1-3. The plan is to attempt to survey the four primary selections and to switch to the backup only if it proves impractical to achieve the quality goals of the projects surveying one or two of the primary choices. If a third backup is required, TSSWCB will be consulted for

changing the project plan. Orthophotos of the four primary and two backup selections are shown in Figures B1-1, B1-2, B1-2, B1-4, B1-5, and B1-6, respectively.

Table B1-1: Properties of FRS and their contributing watersheds within McCulloch County

FRS Name	Longitude (deg)	Latitude (deg)	Date Impounded	Repaired	USLE K*	Relief Ratio	Primary Land Use	Watershed Area (mi.^{2})	C/A (ft)
BC 1	-99.3650	31.0917	1956	X	0.32	0.013	Range-Brush	7.03	0.8295
BC 4	-99.4450	31.0667	1957	X	0.32	0.009	Range-Brush	3.59	0.7564
BC 5	-99.4783	31.0567	1958		0.32	0.010	Range-Brush	4.06	0.6439
BC 6	-99.4717	31.0783	1958		0.32	0.009	Range-Brush	4.49	0.7071
BC 10	-99.5117	31.1183	1957	X	0.32	0.011	Range-Brush	1.40	0.6830
BC 11	-99.5167	31.1033	1958		0.32	0.009	Range-Brush	2.66	0.4353
BC 12	-99.5367	31.0833	1959		0.32	0.009	Range-Brush	2.58	0.7794
BC 13	-99.5533	31.0733	1958		0.32	0.009	Range-Brush	3.44	0.8280
BC 14	-99.5800	31.0717	1956	X	0.32	0.006	Range-Brush	11.52	1.0487
BC 15	-99.577	31.0967	1959		0.32	0.008	Range-Brush	4.57	0.6865
BC 16	-99.6067	31.1233	1959		0.32	0.009	Range-Brush	3.73	0.6585
BC 17	-99.5967	31.1467	1962		0.32	0.004	Range-Brush	28.8	0.7330
BC 39	-99.5600	31.2367	1955	X	0.32	0.009	Range-Brush	4.61	0.6931
BC 40	-99.5267	31.2150	1955	X	0.32	0.011	Range-Brush	1.50	0.6990
BC 41	-99.5100	31.2150	1958	X	0.32	0.008	Range-Brush	8.98	0.6480
BC 43A	-99.4533	31.2150	1960		0.32	0.006	Agricultural	2.98	0.6418
BC 43B	-99.4417	31.2083	1960		0.32	0.011	Range-Brush	6.16	0.6765
BC 44	-99.3550	31.2000	1955		0.32	0.007	Agricultural	2.25	1.1160
BC 45	-99.3483	31.2217	1956	X	0.32	0.006	Agricultural	3.30	0.9361
BC 46	-99.3233	31.2017	1956	X	0.32	0.011	Improved Grass	2.94	1.1262
DC 1	-99.1567	31.2683	1952	X	0.32	0.010	Range-Brush	8.91	0.7990
DC 2	-99.1400	31.2783	1952	X	0.32	0.014	Agricultural	0.95	0.8618
DC 3	-99.1683	31.2833	1952	X	0.17	0.016	Range-Brush	3.28	0.9237
DC 4	-99.1300	31.2950	1952		0.32	0.015	Range-Brush	1.26	0.6549
DC 5	-99.1200	31.3350	1952		0.32	0.011	Range-Brush	4.76	0.7986
DC 8	-99.1400	31.3850	1952		0.24	0.011	Range-Brush	5.41	0.6267
LSS 1	-99.1200	31.2283	1959		0.32	0.012	Range-Brush	2.75	0.4864
SWL 6A	-99.5847	31.2797	1987		0.32	0.013	Agricultural	8.06	0.3838
SWL 7	-99.5583	31.3367	1982		0.32	0.007	Improved Grass	3.70	0.6748
Averages					**0.31**	**0.010**	**Range-Brush**	**5.16**	**0.7426**

FRS within McCulloch County, Texas. FRS name, geographic locations, date of impoundment, watershed area, and floodwater capacity/watershed area ratio are given by or computed from the NID. Repaired are those FRS which had repair work completed through this project. USLE K is the soil erodability factor. *The units of USLE K are 0.013 t m^2 hr/(m^3 t cm). The primary soil USLE K factor, land use, and relief ratio are from SWAT. Tarrant soils are composed of 50% clay, 28% silt, and 22% sand and have a USLE K of with a USLE K of 0.20. Mereta soils are 38% clay, 32% silt, and 30% sand and have a USLE K of 0.32. Speck soils are composed of 30% clay, 37% silt, and 33% sand and have a USLE K of 0.17. Winters soils are composed of 15% clay, 20% silt, and 65% sand and have a USLE K of 0.24.

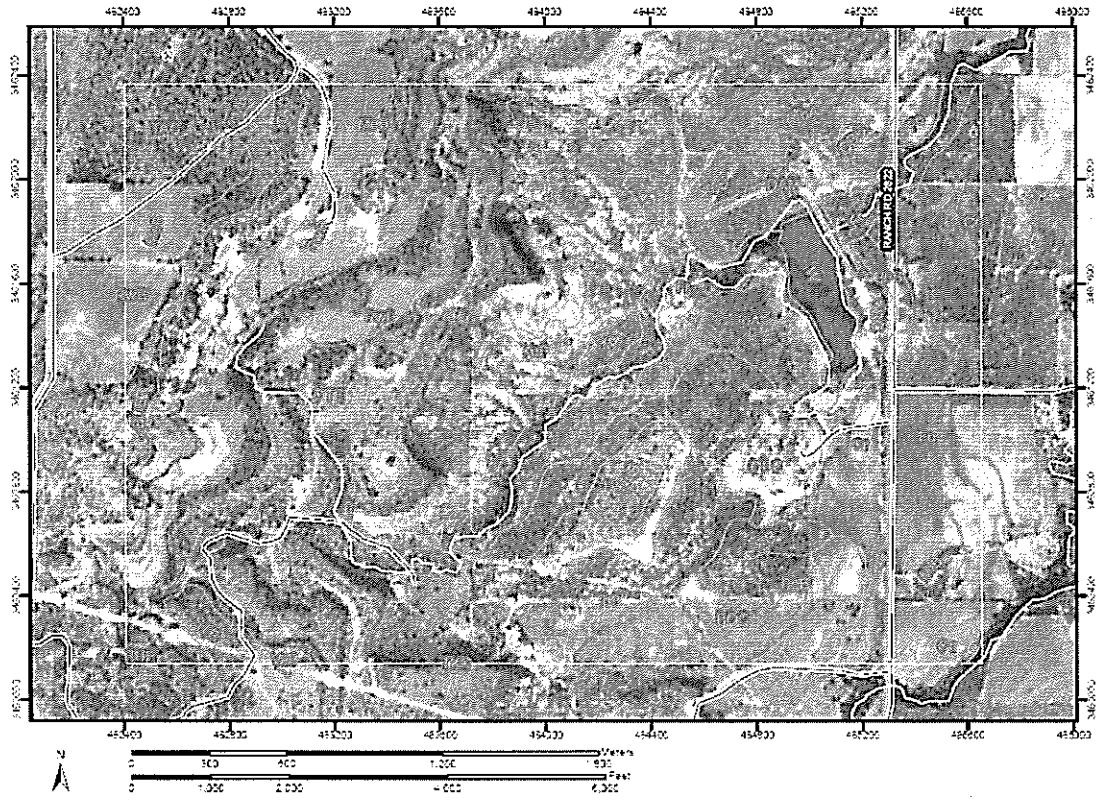
Table B1-2: Primary selections for FRS surveys

FRS Name	Longitude (deg)	Latitude (deg)	Date Impounded	Repaired	USLE K*	Relief Ratio	Primary Land Use	Watershed Area (mi.^{2})	C/A (ft)
BC 1	-99.3650	31.0917	1956	X	0.32	0.013	Range-Brush	7.03	0.8295
BC 39	-99.5600	31.2367	1955	X	0.32	0.009	Range-Brush	4.61	0.6931
DC 3	-99.1683	31.2833	1952	X	0.17	0.016	Range-Brush	3.28	0.9237
DC 8	-99.1400	31.3850	1952		0.24	0.011	Range-Brush	5.41	0.6267
Averages					**0.26**	**0.012**	**Range-Brush**	**5.08**	**0.7683**

Table B1-3: Backup selections for FRS surveys

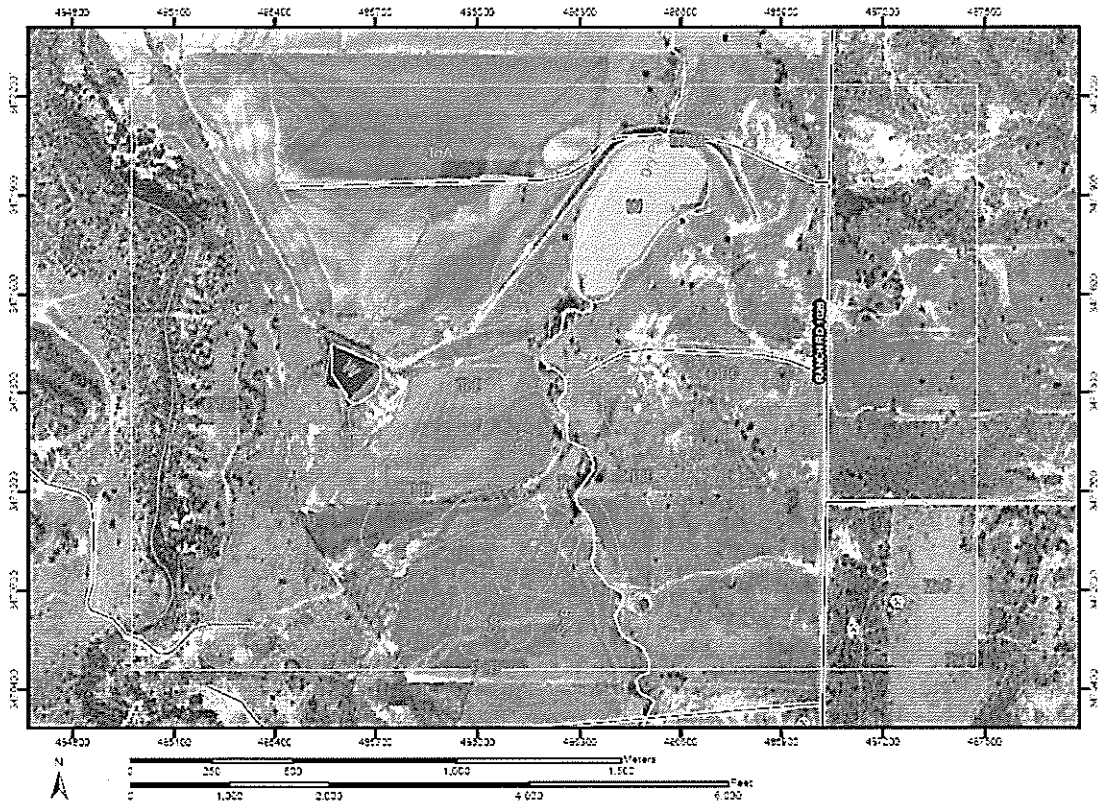
FRS Name	Longitude (deg)	Latitude (deg)	Date Impounded	Repaired	USLE K*	Relief Ratio	Primary Land Use	Watershed Area (mi.^{2})	C/A (ft)
BC 4	-99.4450	31.0667	1957	X	0.32	0.009	Range-Brush	3.59	0.7564
DC 1	-99.1567	31.2683	1952	X	0.32	0.010	Range-Brush	8.91	0.7990
Averages					**0.32**	**0.010**	**Range-Brush**	**6.25**	**0.7777**

Figure B1-1: Orthophoto and soils of primary selection, FRS DC 3



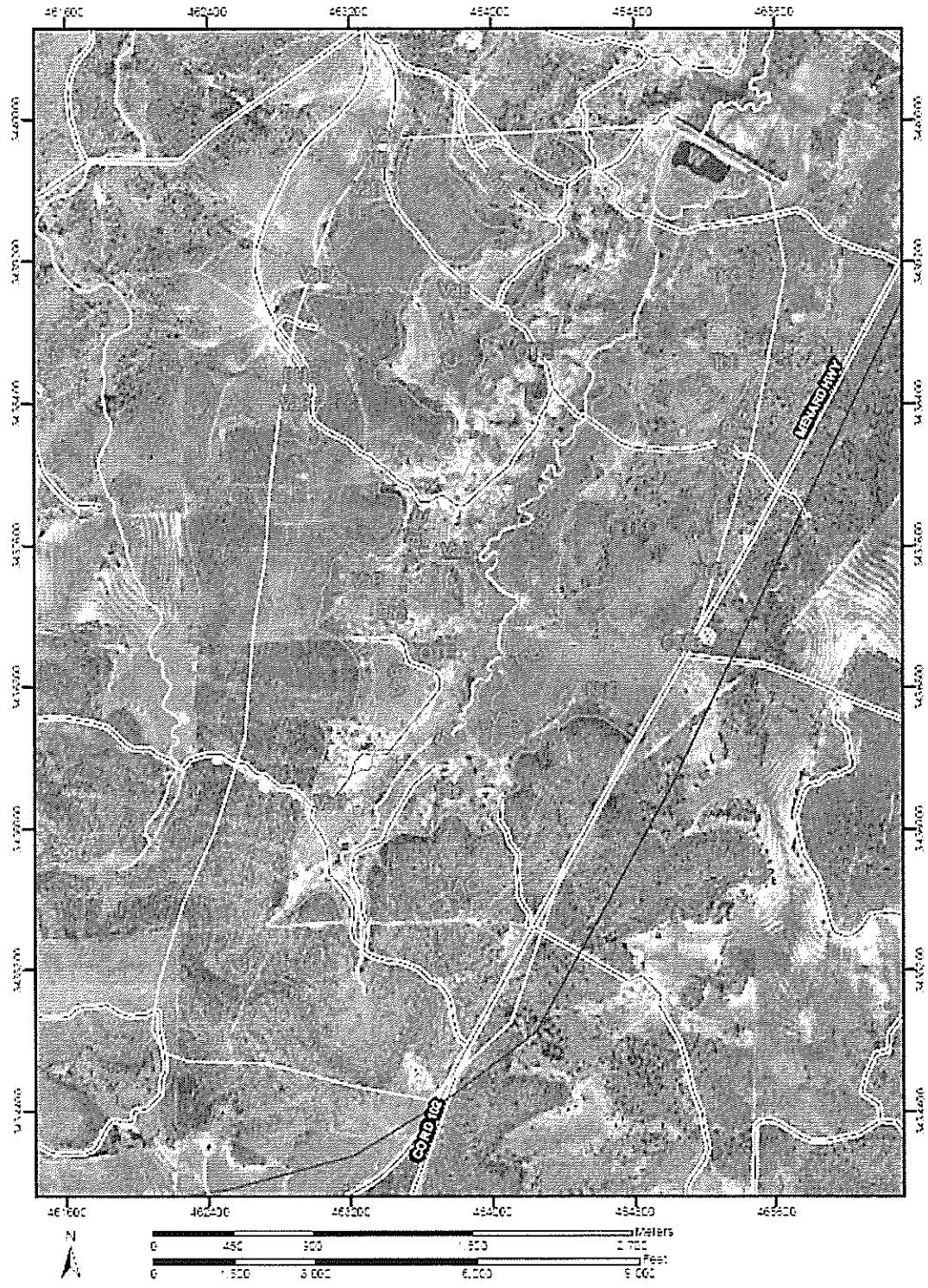
Orthophoto and soils overlay generated by NRCS Web Soil Survey. FRS DC 3 is label W. Soils are labeled as follows: BOC is Bonti-Owns, BUE is Brackett-Tarrant, CMB is Cho-Mereta, Cn is Clairemont silt loam, DAM is Dam embankment, Fo is Frio clay loam, Fr id Frio clay loam, channeled, KuB is Nukrum silty clay, MeB is Mereta clay loam, MfB is Miles fine sandy loam, NuB is Nuvaide clay loam, OBC is Owens-Blanket, OTE is Owens and Tarrant, PeB is Pedernales fine sand loam, RwB is Rowena clay loam, SaB is Sagerton clay loam, STB is Speck and Tarrant, TAC is Tarrant, TKC is Tarrant-Kavett, ToA is Leeray clay 0 to 1% slopes, ToB is Leeray clay 1 to 3% slopes, VaB is Valera clay, W is water. Geographic coordinates are UTM Zone 14, meters.

Figure B1-2: Orthophoto and soils of primary selection, FRS DC 8



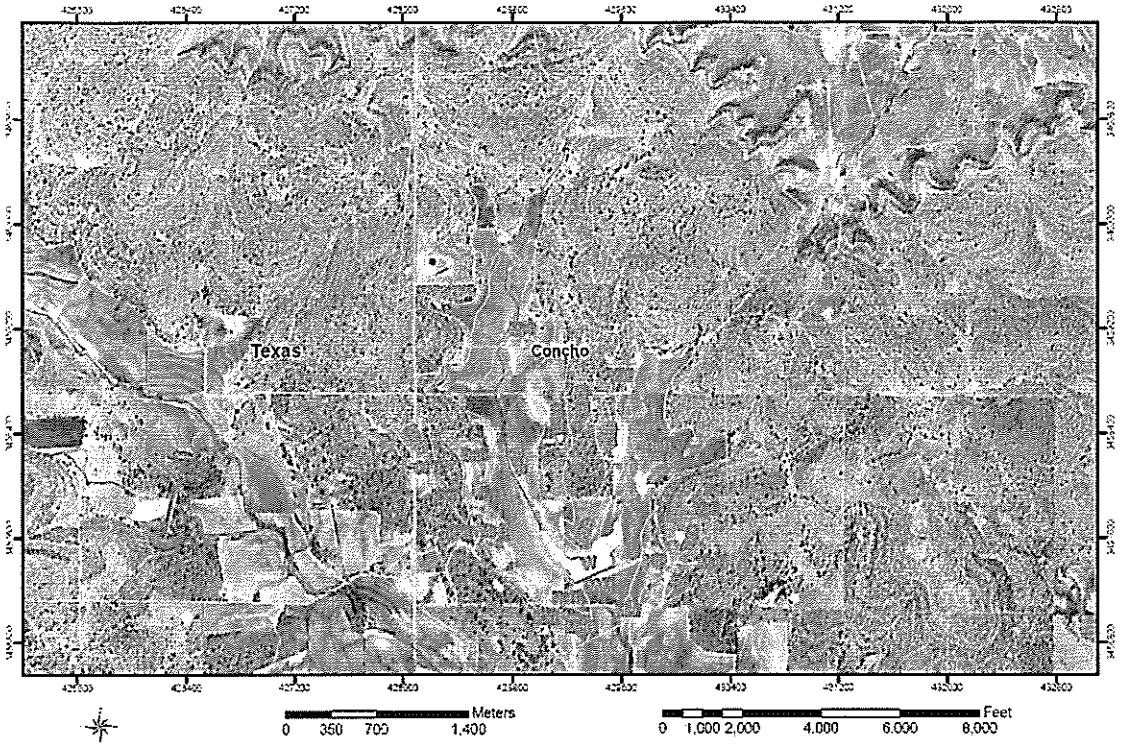
Orthophoto and soils overlay generated by NRCS Web Soil Survey. FRS DC 8 is label W. Soils are labeled as in Figure B1-1. Geographic coordinates are UTM Zone 14, meters.

Figure B1-3: Orthophoto and soils of primary selection, FRS BC 1.



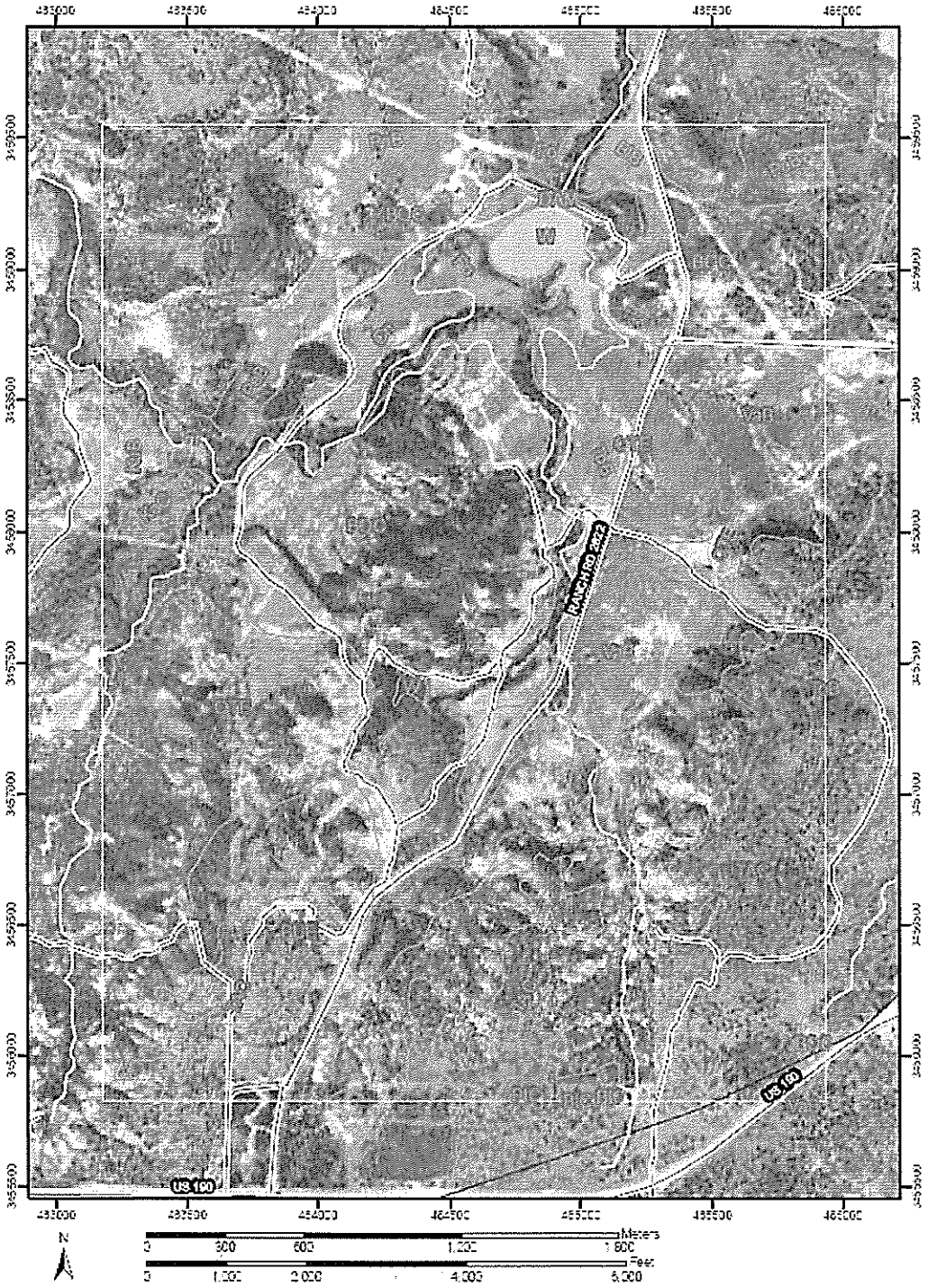
Orthophoto and soils overlay generated by NRCS Web Soil Survey. FRS BC 1 is label W. Soils are labeled as in Figure B1-1. Geographic coordinates are UTM Zone 14, meters.

Figure B1-4: Orthophoto and soils of primary selection, FRS BC 39



Orthophoto and soils overlay generated by NRCS Web Soil Survey. FRS BC 39 is label W. Soils are labeled as in Figure B1-1. Geographic coordinates are UTM Zone 14, meters.

Figure B1-5: Orthophoto and soils of backup selection, FRS DC 1



Orthophoto and soils overlay generated by NRCS Web Soil Survey. FRS DC 1 is label W. Soils are labeled as in Figure B1-1. Geographic coordinates are UTM Zone 14, meters.

Figure B1-6: Orthophoto and soils of backup selection, FRS BC 4

Orthophoto and soils overlay generated by NRCS Web Soil Survey. FRS BC 4 is label W. Soils are labeled as in Figure B1-1. Geographic coordinates are UTM Zone 14, meters.

B1.2 Design of sediment coring program for Project Task 5

Sediment core samples will be collected from the four FRS to be surveyed in McCulloch County, to calibrate acoustically determined sediment thickness, to determine the average dry bulk density of the sediment, and to provide sediment samples for ^{137}Cs and contaminant analyses. The distribution of sediment properties within FRS is potentially much more complex than in conventional water supply reservoirs that are filled to near capacity most of the time. FRS are commonly near empty or dry when the first flush of storm runoff reaches the structure and then progressively fill during the event. Then after the event, they drain slowly over days or weeks back to the normal pool elevation. If no further rainfall occurs for a period, evaporation and leakage gradually reduce the lake level below normal pool level and in some cases may leave the structure completely dry. During this process, wave action at the migrating shoreline can progressively remobilize fine sediment originally deposited in the shallow backwater region and move it further toward the dam. Because contaminants are preferentially adsorbed onto the sediment fines, this process tends to concentrate contaminants in the deeper parts of the structure. As freshly deposited sediment is exposed and dries, it becomes much more compacted than sediment that remains submerged. For these reasons, both the physical and chemical properties of the sediment in FRS tend to vary along the axis of the reservoir. Sediment texture and degree of compaction tend to vary along the axis of reservoirs, with the sediment in backwater regions being coarser and more compacted than that in the deeper regions near the dam. To account for this variation, three core sites will be selected in each FRS reservoir surveyed. One site will be in the deepest water near the dam, one site will be in an intermediate position along the axis of the reservoir and one site will be in the backwater region. This is the same sampling strategy described by Van Metre et al. (2003).

Prior to selecting the specific core sites, the real-time display of the acoustic sub-bottom profiler will be used to survey the general area of the reservoir to be sampled, to find a spot representative of that part of the reservoir. By acoustically targeting core sites, slopes and other local bathymetric anomalies, which may not produce representative sediment samples, can be avoided. Using this approach, fewer cores are required to achieve an adequate sample of sediment properties. Two cores will be collected at each site. One core will be cut open lengthwise to view the stratigraphy intact, for visual inspection and interpretation. The second core will be extruded in 5 cm sub-samples for chemical analysis.

Where there is sufficient water depth to float the survey boat, sediment cores will be collected in the water covered regions of the reservoirs using a submersible vibracoring system that runs on 24-volt DC power supplied by two trolling motor batteries. Nutrients and other contaminants in exposed and dried sediment are subject to vertical migration with meteoric water flowing through the unsaturated zone and uptake by plants. Hence, sediment in the parts of reservoirs that are dry most of the year are potentially poorer recorders of tapped contaminants.

Where necessary, coring the exposed reservoir bottom will require a different approach. A vibracoring system based on a pneumatic fencepost driver will be used for coring on dry land. Because the sediments are dry and compacted, more power is required to drive the core tube into

the sediment. The pneumatic driver essentially hammers the tube into the ground. The land coring system consists of a gasoline-powered air compressor, driver head, and a collapsible tripod with a hand winch for extracting the tube. The system is trailered to the coring site behind a pickup truck. For consistency, other than the method of driving the core, the same thin-walled aluminum or stainless steel core tubes and sample handling procedures will be used in both water and land coring operations. The geographic locations of core sites on water and land will be determined using DGPS. The cores will be sealed and stored in ice in the field and transported to BUDG and stored at 4 °C before sub-sampling.

B1.3 Design of Sediment survey for Project Task 6

The design of the sediment surveys of FRS will be consistent with that described in the USACE hydrographic surveying and sedimentation investigation manuals (USACE, 2001; 1989), except that the profile spacing will be reduced from that recommended in proportion to the reduced size of FRS compared to water supply reservoirs. The goal is to collect the acoustic profiles in the direction of greatest spatial change. The standard practice is to collect acoustic profiles in parallel lines, trending across the long axis of the reservoir, perpendicular to the submerged stream channel (thalweg). Water supply reservoirs, with surface areas of hundreds to thousands of hectares, are typically surveyed with profiles spaced 100 to 500 m apart. FRS, with surface areas of tens to hundreds of hectares, are surveyed with profiles spaced 10 to 50 m apart. Profile lines will be pre-planned and the corresponding line files generated for the HyPack navigation software, such that the entire area of the reservoirs at normal pool elevation is covered. Extra lines and extra line length on either end will be added to make sure the entire area below the elevation of the principal outlet works is sampled.

Adherence to the completeness component of QC will be judged by the percentage of the total line length collected within the normal pool area. A number of factors limit data coverage. To adequately couple the acoustic signal to the water, the acoustic transducer array must be placed at a water depth of at least 40 to 50 cm. This limits the extent of profiles to water depths of 50 cm or more. Also, underwater obstacles, such as aquatic vegetation, rocks, logs etc. limit the area in which the survey vessel can travel. In land-based surveying operations elevation profiles will be at the same spacing as that used in the water covered region of the reservoir. Land-based operations on the ATV are limited to areas that are relatively free of brush, have slopes low enough for safe ATV operation, and ground that is not too wet and soft to support the vehicle. Hence, regions between water depths less than 50 cm and ground dry enough to support a small ATV will not be surveyed. If, on the day of the survey, it appears that the total profile line length that must be dropped due to these and other factors exceeds 10% of the total length within the normal pool area, some adjustment will be required. If the nature of the obstruction preventing data collection is judged to be temporary, then the data that can be collected on that day will be collected. Then, when conditions change, such as the land drying further or the lake level rising, the survey crew will return to fill in the missing data. If the condition is judged to be long-lived or permanent, the survey will be switched to one of the pre-selected backup FRS. If both backup FRS have been surveyed, BUDG will contact TSSWCB to discuss any required changes to the project plan.

Section B2: Sampling Methods

B2.1 Sampling methods for Project Task 5, collecting sediment cores

B2.1.1 Sampling methods by water-based coring

The coring system that will be used for collecting cores in lakes consists of an 24 volt vibracorer from Specialty Devices, Inc. of Wylie, Texas, and an 8 ft, tilt-up, A-frame, coring derrick that is mounted on a large capacity, 14 ft Jon Boat. When outfitted for coring the boat carries two people, an outboard motor, sub-bottom profiling system with integrated DGPS system, the vibracore driver, three 12 volt trolling batteries, two anchors, and 6 core tubes. With this payload, the boat must have sufficient extra buoyancy to pull core tubes up to 12 ft in length out of the bottom. The boat is transported on a trailer with roller rails and 16 ft roller ramps to within 10-15 ft of the shore, the ramps are extended from the back of the trailer, and the fully loaded boat is rolled off the trailer, down the ramps and into the water. The boat is retrieved by winching it back up the ramps and onto the trailer.

Cores will be collected at three general areas in each reservoir surveyed. With the goal of collecting sediment samples that characterize the range of sediment textures and densities within the reservoir, cores will be collected near the dam, at mid lake and in the backwater, as described in Section B1. In preparation for coring, coordinates for the general region of each core site will be selected from orthophotos of the sites (Figures B1-1 through B1-6). The disposable core tubes that will be used will be prepared by cutting the tubes to length and drilling three holes in the tops of the tubes that align with the attachment points on the vibracore driver. Core catchers will be fabricated and installed in the bottom of each tube. Once the tube fabrication is complete, the tubes are washed with borax and water, swabbed, rinsed with distilled water, dried, then rinsed with ethanol, and dried again. Then the tubes receive a final rinse with a 10% nitric acid solution, are rinsed again with distilled water, dried, and the ends sealed in the fabrication laboratory. Two types of core tubes will be used, which are both 3 inches (76 mm) in diameter and have a wall thickness of 1/16 inch (1.5 mm). Aluminum tubes are easily opened by sawing and are therefore used to collect samples that will be cut in half lengthwise and viewed intact for physical description, optical scanning, and stratigraphic interpretation. After examination, these cores will be sub-sampled for water content analysis and the resulting dried samples are powdered and sieved for ^{137}Cs analysis. Stainless steel tubes will be used to collect the samples for the chemical analyses.

The specific core sites within the water-covered areas of FRS will be selected in the field with the aid of the sub-bottom profiler. This will be done by profiling back-and-forth in the general area of the pre-planned core site. The profiler displays the boat's position within the reservoir and an image of the bottom and sub-bottom sediment layers in real time. Core sites will be selected that are relatively level and in which the sediment thickness and acoustic characteristics are typical of that part of the reservoir. To improve the chances of sampling texturally distinct pre-impoundment material, sites in the submerged floodplain are preferred over the submerged

channel. If the core locations were selected blindly, many more cores would be required to characterize the sediment properties.

Once the coring location is selected, the survey boat is held at the core location between two anchors, one upwind and one downwind. To collect a core, the top of core tube is bolted onto the receiving nozzle at base of the vibracore driver. The vibrator is then lowered into the water to a measured depth by hand winch, so that the end of the core tube is approximately 2 ft above the bottom. The vibrator is then turned on and slowly lowered into the bottom, until the full weight of the vibrator is on the tube and no further progress into the bottom is being made. Once the tube has been driven to refusal, the vibrator is turned off and with the tube still in the bottom, a DGPS fix is taken of the core location. The core is then winched out of the bottom and back onto the boat.

The retrieved core is examined to determine if it likely meets the sampling requirements. Evidence of mud on the base of the vibrator driver indicates that the top of the tube was driven into the mud and the top of the sample is likely lost. In this case, a longer tube is attached to the vibrator and another core is collected. Evidence of mud on just one side of the vibrator driver indicates that the vibrator fell over at some point during the coring process and another core is required. In cases in which the sediments are clay-rich and have been dried to a low moisture content in the past, the underwater vibrator will not penetrate. In such cases, the site must be abandoned and a new site in which the sediments are not as compacted is sought. If mud is caked part way up the tube, the bottom of the core is examined to see if it contains pre-impoundment material. If the bottom of the core is soft sediment, then it is likely that the pre-impoundment was reached but was too hard to be sampled. If the core passes this initial inspection, the tube is detached from the vibrator, capped at the bottom, and then probed with a rod from the top to determine the depth to the top of the sediment in the tube. Pipe cutters are used to trim the core tube at the mud line and the top is capped.

Once all the cores have been collected at a given site, the anchors are pulled and an additional acoustic profile is collected through the core site. This is done to tie the acoustic data to the coring results. To navigate over the core site, the core location is entered into the Hypack navigation software as a target and the program guides the pilot back to the location as an acoustic profile running through the core site is collected. In this way, co-located acoustic data and cores can be collected to within the navigational accuracy (±1 m). After all the cores have been collected for a given reservoir, the cores will be taken to shore and placed in ice for transport to the BUDG laboratory.

The underwater vibracoring system is designed to penetrate soft sediments. In cases in which the sediment is clay-rich and has been thoroughly dried in the past, this system may not penetrate the sediment. The goal for this coring operation is to collect at least one core in each FRS that penetrates the complete post-impoundment section and samples the pre-impoundment material. In cases in which this is not possible in the water, core sites will be located on land and a land-based coring system will be used.

B2.1.2 Sampling methods by land-based coring

Vibracore systems driven by electric motors are effective tools for collecting cores of soft, high water content sediment, but these systems commonly fail to penetrate clay-rich sediment that has been dried and compacted. For coring on land, BUDG uses a pneumatic core driver that essentially hammers the tube into the ground. The land coring system consists of a gasoline-powered air compressor, pneumatic driver head, and a trailer-mounted tripod with a hand winch for extracting the tube. The system is trailered to the coring site behind a pickup truck. The specific core sites are chosen in the same way as in the water-based coring, except that the site selection is based on visual inspection of the landscape. The same thin-walled aluminum or stainless steel core tubes and sample handling procedures will be used in both water and land coring operations. Cores are collected by sliding the pneumatic driver over the top of the core tube, standing the tube and driver up vertically at the core site, and turning on the driver. The driver is allowed to drive the tube into the ground until no further progress is made. Then the driver is turned off and slid off the top of the tube. The top of the tube is connected to the hand wench cable and pulled out of the ground. The geographic locations of core sites on water and land will be determined using DGPS. Both types of cores will be sealed and stored in ice in the field and transported to BUDG and stored at 4 °C before sub-sampling.

B2.1.3 Core sub-sampling and sample handling methods

In the BUDG core laboratory, the sediment cores collected in aluminum tubes will be analyzed to determine the thickness of post-impoundment sediment, the average dry bulk density of the sediment, using analytical methods described in Section B4. The aluminum core tubes are opened by sawing through the core wall lengthwise on both sides and then cutting the core in half, longitudinally. This leaves the core intact, with the undisturbed center open to view. Viewing the entire undisturbed core at once aids visual identification of layering within the cored material. The cross-sectioned core is described, photographed, and sub-sampled nominally in 5 cm increments, using pre-cleaned stainless steel implements and bowls. Variations to the regular sub-sample increments are made to place sample boundaries at abrupt layer boundaries, where present. Measured volumes of sub-samples from the other half are weighed wet and then again after drying at 106 °C for 24 hours.

The longest and/or most complete core from each FRS will be selected for ^{137}Cs analysis. To prepare for ^{137}Cs analysis, the dried sub-samples from the aluminum tubes are ground to powder and passed through a number 20 sieve (850 μm). Then 25±0.2 g portions from each 5 cm sub-sample are sealed in 50x9 mm polystyrene Petri dishes for ^{137}Cs analysis. Polystyrene Petri dishes of this size are used to match the geometry and container type of BUDG's ^{137}Cs standard. Other container types could be used, but each container type requires a standard of matching geometry.

The cores collected in stainless steel tubes will be used to supply composite samples for chemical analysis. Soft sediment cores will be extruded from the core tubes using a plunger and sub-sampled in 10 cm increments. Compacted sediment cores and cores from land will be cut in 10 cm increments using a tube cutter. Each sub-sample will be thoroughly mixed. Then 50 g

portions from each sub-sample within the core will be combined and thoroughly mixed to form a composite sample for the entire core. Three composite cores will be generated from each of four reservoirs to produce 12 primary samples. In addition, one core will be selected from each reservoir to generate a laboratory sample slit (33%). Hence, there will be 16 total composite samples generated. Half of each composite sample will be placed in an oven and dried at 106 °C for 24 hours and placed in pre-cleaned and certified Type III glass sample jars with Teflon-lined polypropylene lid. These dried composite samples will be transferred to the CRASR lab for organic carbon and nutrient analyses. Similarly, the remaining half of the wet composite sample will be sealed in Type III glass jars without drying, placed back under ice at 4 °C, and transferred to the GERG lab for trace metal and pesticide analyses.

Table B2-1 Sediment core and sub-sample parameters

Core tube type	Ethanol and acid-washed Aluminum	Ethanol and acid-washed Stainless steel
Sample analysis	^{137}Cs	Organic Carbon, Nutrients, trace metals, pesticides
Sub-sample containers	50x9 mm polystyrene Petri dishes*	Pre-cleaned, I-CHEM certified, Type III glass sample jars with Teflon-lined lids
Minimum sample mass	25 g	50 g
Preservation	Oven drying	Maintained at 4 °C before sub-sampling, frozen after sub-sampling
Holding time	-	28 days for Organic carbon and nutrients, 6 weeks for metals, one year for pesticides

Sample collection device cleaning procedures are taken from EPA-823-B-01-002, page 3-14.
Sample holding times are taken from EPA-823-B-01-002, Table 4-1.
Sample container standards are from EPA SOP #2016, 1994.
*Note: The standard sample container for gamma-ray spectrometry is the Marinelli beaker, which raps around and over the counter and provides the most efficient geometry for gamma ray detection. However, Marinelli come in 0.5, 1, 2, and 4 L sizes, which are too large for the amount of sample produced from core sub-samples (25 to 50 g). In their product documentation at http://www.canberra.com/pdf/Products/, Canbarra, Inc. suggests using plastic Petri dishes as containers for gamma-ray counting for small samples. This is the approach adopted by BUDG.

B2.2 Sample methods Project Task 6, sediment surveys

Modern sediment surveys are conducted in water supply reservoirs by traversing the reservoir along parallel profiles in a survey vessel equipped with an acoustic fathometer and a DGPS positioning system (USACE, 2001). The data collected in reservoir surveys are used to map the bathymetry of the reservoir and compute the water storage capacity at the normal pool elevation. The volume of post-impoundment sediment is then inferred indirectly from the apparent change in water capacity between the time of impoundment or a previous survey and the current survey. This approach relies on the reservoir being filled nearly to the normal pool elevation, which is commonly not the case in FRS. Some FRS in McCulloch Country are completely dry most of the year, whereas others are only partially filled. For FRS surveys, BUDG augments the normal water-based survey method with dry-land surveying and coring, as necessary to achieve complete data coverage within the reservoirs. The following sections describe the various components of the surveying systems that will be used and associated sampling methods.

B2.2.1 Water depth and sediment thickness surveying

The water-based surveying methods used by BUDG are similar to the standard methods used in large water supply reservoirs, except that the equipment is miniaturized for use in two-person boats that can be deployed in small lakes and ponds and a combination of high- and low-frequency acoustic signs is used to map both the water bottom and base of sediment (200, 125, 50, 25 and 12 kHz). In addition, full-waveform digital recordings of the acoustic profiles are made during the survey so that the water bottom and base of sediment can be manually traced on the data during post-survey processing. This is normally not done in standard bathymetric surveys, but is particularly important in shallow, vegetated reservoirs. Under these conditions, conventional fathometers commonly record travel times for multiple reflections within the water column and reflections from vegetation as often as they record the direct reflection from the water bottom, resulting in significant error in the water depth measurements.

The acoustic profiling instrument measures the depth to the water bottom, relative to the water surface. Depending on wave conditions, the point-to-point accuracy of these measurements can at times be limited to no better than ±20 cm. However, because waves oscillate about the current water level, the bias in these measurements is typically on the order of ±3 cm (USACE, 2001, Chapter 4). It is the bias that limits the accuracy of the computed water volume. To convert these measurements to water depth relative to the outlet works elevation, it is necessary to measure the elevation difference between the water surface on each day of the survey and the outlet works. In most FRS, the primary outlet works are standing pipes or concrete columns in the water immediately in front of the dam. If water is present along the standing outlet, the vertical distance from the lip of the outlet works to the water level is measured with a leveling rod. If the water level is below the base of the outlet, the difference in elevation is measured by leveling with conventional optical surveying instruments.

Acoustically mapping the sediment thickness with low-frequency signals makes it possible to determine the sediment volume directly, without reference to prior surveys. Acoustic sediment thickness measurements are validated by collecting co-located sediment cores. The bathymetric measurements will be used to map water depth and compute the remaining reservoir storage capacity at the design pool elevation. The sediment thickness measurements will be used to map sediment thickness within the reservoirs and to compute the volume of trapped sediment. It is not always possible to image the base of sediment acoustically. In cases in which the bottom has be repeatedly exposed and dried, there may be too little acoustic contrast between the sediment and the pre-impoundment soil for the sediment layer to be mapped. Also, in situations in which the water depth is less than the sediment thickness, multiple reflections of the acoustic signal in the water column obscure the reflection from the base of sediment. In these cases, the sediment volume will be determined by the standard method, from the change in water volume from either the as-built reservoir volume or the volumes determined by prior surveys.

Water-based sediment survey methods are logistically more efficient and accurate than land-based methods. Hence, the use of water-based methods will be maximized in the surveys of FRS in McCulloch County. For this reason, the field operations will be on the water during fall 2007

and winter 2008, when the reservoirs are likely to be filled to the highest levels of the year. Cores from the submerged parts of the reservoir can be collected at the same time the sediment surveys are conducted. The land-based surveying and coring operations require completely different equipment, and are most practical when the reservoir water levels are low. Hence, the land survey and coring in the exposed portions of the reservoir bottom will be done in separate trips during the early fall 2007, when water levels in the reservoirs are normally lower than in the winter and spring. Hence, multiple trips between BUDG and McCulloch County will be required to survey and core all four reservoirs. The physical analysis and sub-sampling of the cores for each reservoir will be done within 7 days after each trip (Table B2-1). Post-survey data processing, acoustic data analysis, and mapping will begin during this same timeframe and will be completed during the winter of 2008.

The sub-bottom profiling system that will be used in the water-based survey component includes a built-in DGPS navigation system. Position data will be used in real-time to provide navigation information to the vessel operator. The helmsman will be presented with a plan view of the survey area with the vessel position and track. A color-coded track-line of the sonar coverage is painted to the screen and used to navigate the survey vessel along a pre-planned route. To check the accuracy of the positioning system and confirm that the geodetic parameters used in the real-time projection to the NAD83, Texas State Plane Central Zone coordinate system are correct, a position check will be conducted daily on an established monument with a known position. The monument that will be used is the only third order Benchmark listed in the National Geodetic Survey's database within 10 miles of Brady, Texas. This is monument CA1092, located at 31 03 21.68820 N, 99 14 57.02046 W, which is 8 miles south of Brady, on Ranch Road 734. All vertical coordinates will be measured relative to the elevation of the primary outlet works of the reservoirs to determine the water depth when filled to the normal pool elevation. The acoustically measured water depths and depths to the base of sediment are made relative to the water surface. Hence, the water surface elevation relative to the outlet works will be measured daily, using the methods described previously in this section. All soundings will be reduced to feet (ft) of depth relative to the outlet works elevation in the delivered data set.

In acoustic profiling, it is not critical that the lines are straight or spaced at exactly the planned spacing. Instead, it is more important to insure that there are no large gaps between profiles and that there are no unsampled regions of the reservoir. Uniform spatial sampling will be achieved by pre-planning the profile lines and then following those lines during the survey. The survey lines are planned by first digitizing the shoreline on digital orthophoto quarter quads (DOQQs) from TNRIS. The shoreline is imported into Hypack™, a standard hydrographic surveying software package from Hypack, Inc of Middletown, CT. In the surveying planning section of Hypack, regularly-spaced, parallel survey lines are pre-planned to fill the reservoir area. FRS vary significantly in water level and some reservoirs in the study area will likely be completely dry during the survey. For this reason the digitized shoreline is used as a guide for profile line planning purposes and as a reference during surveying, but will not be used as part of the survey. For FRS that are dry on the DOQQs, the general area typically occupied by the reservoir will be judged based on vegetation patterns. In both cases, the planned lines will be extended well beyond the limits of the apparent reservoir. Then during the survey, the Hypack survey program displays the real-time position of the survey vehicle on the profiler screen along with the mapped

shoreline and planned profile lines. Navigation aids within the Hypack program indicate the current distance to the right or left of the current line as the boat is piloted along the pre-planned lines. The vehicle speed will be kept below 3 MPH to achieve adequate sampling along the profiles.

B2.2.2 Land elevation surveying

Because FRS in McCulloch County are typically only partly filled or completely dry year around, land-based surveying operations will be required. The land-based equivalent to a bathymetric survey measures the topographic elevation of the exposed reservoir bottom relative to the outlet elevation using GPS. The conventional DGPS used to determine horizontal position in the water-based survey is limited in vertical accuracy to ±3 m, which is insufficiently accurate for use in surveying the elevation of the reservoir bottom. For this reason, a second kind of GPS system, real-time kinematic (RTK) GPS will be used to measure the land surface elevation in the dry portions of the reservoirs. In RTK GPS navigation, carrier phase measurements of the GPS signals are used to correct the GPS positions in real time to an accuracy of 1-2 cm horizontal and 2-3 cm vertical (USACE, 2001, Chapter 16). Two RTK units are deployed and connected by a radio link. One system is left at a fixed reference location, the reservoir outlet works in this case, and the other station is mounted on a mobile survey vehicle. In the current project, the mobile RTK unit will be mounted on an ATV with the antenna held at a fixed height above the ground surface. As the ATV is driven along profiles across the dry reservoir bottom, the RTK system will measure and record the geographic position and elevation difference between the mobile and fixed station. These data will be used to map the reservoir depth and compute the remaining reservoir storage capacity the reservoir would have when filled to the normal pool elevation. In cases in which the reservoir is partially filled, the land-based measurements will be combined with the water-based measurements to produce the normal pool bathymetric maps over the entire reservoir and to compute total storage volumes.

B2.3 Recording Data

All field and laboratory personnel follow the basic rules for recording information:

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

B2.4 Failures in Sampling Methods Requirements and/or Deviations from Sample Design and Corrective Action

Sampling errors occur in cases in which cores do not extend through the complete sediment column. This can happen when the top of the core tube and vibrator head penetrate below the water bottom. This is indicated by the presence of mud on the vibrator head. In this case, the top of the sediment core, at the water bottom will have been forced out of the top of the core tube and will be missing from the core sample. This can happen if the sediment column is thicker than was estimated from the real-time acoustic readings or if the tube penetrated too far into the

pre-impoundment material. Usually, it is possible to tell which of these causes is at fault by examining the mud on the outside of the core tube. In terms of penetrating the pre-impoundment material, all that is needed is enough of a sample to verify that the pre-impoundment surface is reached. If there is excessive penetration of the pre-impoundment material, a second core is collected using a shorter vibration time. If the pre-impoundment surface was not reached, a second core is collected using a longer core tube. If this occurs for the longest available core tube, 3.7 m, a new core location with a thinner post-impoundment layer is selected using the acoustic profiler.

Failures to collect complete sample cores also occur in cases where previous exposure has left fine-grained sediment too hard to be penetrated using the submersible vibracore device. This situation is indicated when the sediment column shown by the acoustic profiler is thicker than the penetration achieved by the vibracore. In these cases, the only remedy is to move to deeper water, where the exposure time is generally less. It is also possible to move to the adjacent shore and core currently exposed sediment using the more powerful pneumatic vibracore system. In unforeseen cases in which none of these normal remedies work, it is the responsibility of the Field Supervisor, to ensure that the actions and resolutions to the problem are documented and that records are maintained in accordance with this QAPP. The Field Supervisor, in consultation with the CRASR QAO and the TSSWCB QAO, will determine if the deviation from the QAPP compromises the validity of the resulting data. Resolution of the situation will be reported to the TSSWCB in the next quarterly report.

Section B3: Sample Handling and Custody

B3.1 Handling of Sediment cores

Sediment cores will be handled following the general procedures described in Section 4 of *Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual (EPA-823-B-01-002)* (EPA, 2001). To achieve integration between acoustic and core data, the cores will be collected at the same time as the acoustic surveys are conducted. However, because the cores need to be placed in ice as soon as possible after collection, they will be collected at the end of the day, after the sediment survey has been completed. As the cores are collected, they will be labeled and sealed on the top and bottom with 3-inch diameter core caps and temporarily stored upright on the boat. Once onshore, the top of the core tube is probed with a metal rod with a flat disk welded to its end, to determine the location of the top of the sediment in the core tube. The core tube is then cut off at the top of the sediment and re-capped. Removing the water-filled section of tube above the sediment prevents the soft sediment from flowing within the core tube and makes it possible to transport the tube horizontally. The trimmed tubes are then placed in a 6 ft long Styrofoam cooler and covered with ice for transport back to BUDG. Cores that are longer than the cooler are cut in half and the halves are capped and labeled. Cores collected on dry land will be handled in the same way as those collected in water, except that any open air space above the top of the core will be removed prior to sealing the core.

B3.2 Acoustic profile data

During the sediment survey, the profiling system records in binary form, the geographic location at which each acoustic trace is recorded, the instrument settings, time of day, and estimated water depth, along with the digitized acoustic returns. The resulting computer files from a single FRS survey are typically 1 gigabyte or more in size. At the end of each survey day, these files are downloaded from the field instrument onto a USB Flash memory drive, as a second copy. The original files are kept on the hard drive of the field instrument until all the data from the survey have been transferred to a second computer and archived on DVDs. A different flash memory device is used to store the files from each survey day. Using this approach, the most likely event that could cause loss of data is for a hard disk failure to occur in the field instrument before the data have been downloaded. In such cases, the only remedy is to replace the hard drive and re-collect the data.

B3.3 Kinematic GPS data

In the dry portions of FRS the elevation of the land surface will be measured with a real time kinematic (RTK) GPS. These systems record the horizontal position and elevation (x, y, and z) in ASCII format. Data volumes expected will be in the range of 10s of megabytes per FRS survey. These data will be downloaded from the field instrument, stored and archived in the same way as the acoustic profile data, described above.

B3.4 Chain-of-Custody

Proper sample handling and custody procedures ensure the integrity of samples from the time of sampling and continuing through transport, sample receipt, preparation, and analysis. In this project the same BUDG personnel will collect, transport, sub-sample and prepare the samples for analysis. The ^{137}Cs analysis will be done by BUDG. For this analysis, no custody transfers will be made. Analysis of carbon and nutrient content of the sample will be done at the CRASR Laboratory. Analysis of trace metals and pesticides will be done at the GERG Laboratory. A Chain-of-Custody form that will be used to transfer samples to the two labs is shown in Appendix N. If unforeseen problems in sample handling or preservation occur, they will be noted by the QAO and replacement samples will be used. The sole exception will be a set of sample splits that will be sent to USDA-ARS in Temple, Texas for quality assurance comparisons. These samples will be supplied in labeled sample containers, together will a hardcopy listing the samples transferred. BUDG will store sealed, 25 g, dry powder, ^{137}Cs samples at room temperature for five years. The analysis performed at the CRASR and GERG laboratories will result in the destruction of the samples.

B3.5 Sample Labeling

Sediment cores will be labeled by writing on the core tube in the field with a Sharpie™. The cores will be identified by the reservoir in which they were collected, the core number within the reservoir (1, 2, 3, etc.), the date of collection, and the top and bottom ends of the core tube. Multiple cores collected at a given location will also be assigned a letter designation (A, B, C, etc.). Core segments that will be cut into halves for transport, will be assigned segment numbers and labeled "bottom" and "top". During core analysis, the core sub-sampling process generates both dry and wet sub-samples. Both types of sub-samples will be stored in pre-cleaned, I-CHEM certified, Type III glass sample jars with Teflon-lined lids. The sample jars are labeled by reservoir name, core number and letter, sub-sample number, the depth interval within the core from which the sub-sample was taken, and the date on which the sub-sample was taken.

Digital acoustic records collected during sediment surveys are labeled using the following labeling convention. All the profiles collected in a given survey are stored in a separate directory with the name of the reservoir surveyed. Individual profiles are stored in separate files with numerical (integer) file names, which list the year, month, day, in which the file was recorded, and the file number collected on that day. Each entry forms a two-digit part to the integer name. For example, the ninth profile collected on May 11, 2007 would be stored in a file named 07051109.bin. The "bin" file type indicates the binary format of the file.

B3.6 Sample Handling

BUDG archives digital acoustic data from sediment surveys on DVDs for long term storage. Two copies are made and stored in separate locations. Once the data has been successfully transferred to DVD and tested, the original field recordings, stored on the field instrument's hard drive are erased.

Cores collected in the field will be transported to BUDG under ice. At BUDG, the cores will be stored at 4 °C until they are sub-sampled. The core sub-sampling process produces both dry and wet sediment samples. The wet samples are immediately placed back under refrigeration at 4 °C. The samples to be dried are placed in a drying oven at 106 °C for 24 hours and then stored at room temperature. Dry composite samples will be transferred to the CRASR Laboratory for organic carbon and nutrient analysis. Wet composite samples will be transferred to GERG for trace metal and pesticide analysis. Unused sub-samples will be stored under appropriate conditions until the holding time for these samples has expired.

Section B4: Analytical Methods

B4.1 Analytical methods used in sediment sample analysis

B4.1.1 Sediment water content and dry bulk density

One of the main goals of the project is to estimate the amount of sediment trapped by FRS in McCulloch County. Normally sediment surveys are designed to produce estimates of in place sediment volumes, but a more useful quantity for determining the impact on water quality is the dry mass of the sediment solids. The dry sediment mass is determined by multiplying the total volume of in place sediment (wet) times the dry bulk density of the sediment (mass of dry solids divided by the volume of the wet sediment). The dry bulk density of the sediment is computed from the water continent using the relation (Santschi et al., 1999)

$$\rho_{db} = \frac{\rho_w \rho_s (1 - wc)}{\rho_s (wc) + \rho_w (1 - wc)}, \tag{B4-1}$$

where ρ_{db} is the dry bulk density, ρ_w is the density of water, wc is the water content by mass and ρ_s is the average density of the sediment solids.

The water content by mass of the sediment is determined from the core samples by weighing a sub-sample wet, drying the sample for 24 hours at 106 °C and then weighing the sample again after it is dry. The water content is then given by the fractional change in the mass of the sediment sample from its wet to dry state

$$wc = \frac{m_{wet} - m_{dry}}{m_{wet}}, \tag{B4-2}$$

where m_{wet} is the mass of the sediment sample in its field condition and m_{dry} is the mass of the same sample after drying. This is ASTM Standard Method D2216-92, as defined in ASTM Standards Volume 04.08 – Construction, Soil, and Rock.

The density of the siliceous sediment solids fraction is computed from the density of the primary components, mineral sediment grains and organic carbon. The sediment mineral grains are composed of quartz, which has a density of 2.65 g/cm^3, and clay, which ranges in density from 2.6 to 2.7 g/cm^3. Hence, an average mineral grain density of 2.65 is assumed. Solid grains of pure Carbon without pore space have a density of 2.25 g/cm^3. The average solids density is then given by

$$\rho_s = 2.65(1 - OC) + 2.25OC, \tag{B4-3}$$

where *OC* is the organic carbon weight fraction produced by the analytical method described in Appendix B.

Using this approach one can determine the dry-weight density of a sample to well within 1%.. The problem is the sample variability, both within cores and between cores. Water contents commonly vary vertically within a core from 75 to 80% at the top to 25 to 35% on the bottom. This can correspond to dry-weight densities that range from 300 kg/m^3 to 1500 kg/m^3. The average dry-weight density of the sediment column is estimated by averaging the dry-weight densities determined for each 5 cm sub-sample. Because some cores contain previously exposed sediments and others do not, the average dry-weight densities can also vary substantially from core to core. This variability is accounted for by dividing the reservoir area into shallow, mid, and deep-water depth components and multiplying the average dry-weight densities from cores in each region by sediment volume in the region. The contributions from each region are then summed to compute the total mass of dry sediment.

B4.1.2 Analytical methods for ^{137}Cs data

BUDG will use the ^{137}Cs method to identify the 1954 and 1964 time lines in one core from each reservoir surveyed. The core that appears to contain the finest-grained sediment and most complete record of sedimentation will be selected for dating. This will normally be the core from the deepest part of the reservoir. The ^{137}Cs technique is a standard method for identifying age lines in sediment cores that correspond to changes in fallout rates of atmospheric ^{137}Cs in the last 50 years (Van Metre et al. 2003; 2004). ^{137}Cs is a component of radioactive fallout from atmospheric nuclear tests in the 1950s and 1960s, which has a half-life of 30.2 yr. Significant fallout of radioactive ^{137}Cs began in North America in 1954 ± 2 yr and reached a peak in 1964 ± 2 yr (Ritchie, 1998). Of the FRS in McCulloch County, 6 were impounded in the early-1950s, 7 in the mid-1950s, 11 in the late-1950s, 4 in the early 1960s, and 2 in the 1980s. So, the majority of FRS in McCulloch County were impounded in the mid- to late-1950s. The date of impoundment will be an additional criterion used to select the reservoirs to be surveyed, as described in Section B1. To the extent possible, reservoirs impounded in the early to mid-1950s were chosen. The older reservoirs are favored for several reasons. They provide a longer record of sedimentation. The presence of detectable concentrations of ^{137}Cs in sub-samples of the cores will indicate post-impoundment deposition, and identification of the 1964 peak in ^{137}Cs in the cores will make it possible to compare sedimentation rates from impoundment to 1964 and from 1964 to present.

^{137}Cs is identified by the characteristic energy of the emitted gamma rays (661.65 KeV). ^{137}Cs concentrations in sediment cores are determined by placing dried, powdered, sieved, and weighed samples in a gamma ray counter for 12 to 24 hours, depending on sample size. The samples are typically taken in 5 cm increments along sediment cores to determine the ^{137}Cs concentration versus depth in the core. Analysis of ^{137}Cs distribution within sediment cores from FRS in Texas and Oklahoma indicate that the onset of ^{137}Cs occurs abruptly rather than gradually within 5 cm sub-samples. The ^{137}Cs analysis for this project will be done at the BUDG Laboratory using a Canberra model GC2520 gamma ray detector equipped with a Canberra

where *OC* is the organic carbon weight fraction produced by the analytical method described in Appendix B.

Using this approach one can determine the dry-weight density of a sample to well within 1%.. The problem is the sample variability, both within cores and between cores. Water contents commonly vary vertically within a core from 75 to 80% at the top to 25 to 35% on the bottom. This can correspond to dry-weight densities that range from 300 kg/m^3 to 1500 kg/m^3. The average dry-weight density of the sediment column is estimated by averaging the dry-weight densities determined for each 5 cm sub-sample. Because some cores contain previously exposed sediments and others do not, the average dry-weight densities can also vary substantially from core to core. This variability is accounted for by dividing the reservoir area into shallow, mid, and deep-water depth components and multiplying the average dry-weight densities from cores in each region by sediment volume in the region. The contributions from each region are then summed to compute the total mass of dry sediment.

B4.1.2 Analytical methods for ^{137}Cs data

BUDG will use the ^{137}Cs method to identify the 1954 and 1964 time lines in one core from each reservoir surveyed. The core that appears to contain the finest-grained sediment and most complete record of sedimentation will be selected for dating. This will normally be the core from the deepest part of the reservoir. The ^{137}Cs technique is a standard method for identifying age lines in sediment cores that correspond to changes in fallout rates of atmospheric ^{137}Cs in the last 50 years (Van Metre et al. 2003; 2004). ^{137}Cs is a component of radioactive fallout from atmospheric nuclear tests in the 1950s and 1960s, which has a half-life of 30.2 yr. Significant fallout of radioactive ^{137}Cs began in North America in 1954 ± 2 yr and reached a peak in 1964 ± 2 yr (Ritchie, 1998). Of the FRS in McCulloch County, 6 were impounded in the early-1950s, 7 in the mid-1950s, 11 in the late-1950s, 4 in the early 1960s, and 2 in the 1980s. So, the majority of FRS in McCulloch County were impounded in the mid- to late-1950s. The date of impoundment will be an additional criterion used to select the reservoirs to be surveyed, as described in Section B1. To the extent possible, reservoirs impounded in the early to mid-1950s were chosen. The older reservoirs are favored for several reasons. They provide a longer record of sedimentation. The presence of detectable concentrations of ^{137}Cs in sub-samples of the cores will indicate post-impoundment deposition, and identification of the 1964 peak in ^{137}Cs in the cores will make it possible to compare sedimentation rates from impoundment to 1964 and from 1964 to present.

^{137}Cs is identified by the characteristic energy of the emitted gamma rays (661.65 KeV). ^{137}Cs concentrations in sediment cores are determined by placing dried, powdered, sieved, and weighed samples in a gamma ray counter for 12 to 24 hours, depending on sample size. The samples are typically taken in 5 cm increments along sediment cores to determine the ^{137}Cs concentration versus depth in the core. Analysis of ^{137}Cs distribution within sediment cores from FRS in Texas and Oklahoma indicate that the onset of ^{137}Cs occurs abruptly rather than gradually within 5 cm sub-samples. The ^{137}Cs analysis for this project will be done at the BUDG Laboratory using a Canberra model GC2520 gamma ray detector equipped with a Canberra

BUDG, this is done using an interpretation program *Depthpic*, which reads and displays the acoustic profiler binary files. The user traces the water bottom and sub-bottom surfaces by drawing on the displayed acoustic data using the computer mouse. The water temperature and conductivity measurements versus depth are used to compute the average speed of sound in the water column and this information is supplied to *Depthpic*, which uses it to convert the signal travel time into depth. Then the depth and horizontal position of each interpreted point is exported to a file that can be read by mapping programs.

The signal frequencies used in the sediment survey were chosen to penetrate soft, high-water content reservoir fill but not the harder, more compacted pre-impoundment alluvium and floodplain soils. Hence, given sufficient penetration, the post-impoundment sediment appears as a continuous layer below the bottom (Figure B4-1). The base of this layer is traced continuously along the profiles.

Figure B4-1. Example acoustic profile of reservoir bottom and sub-bottom

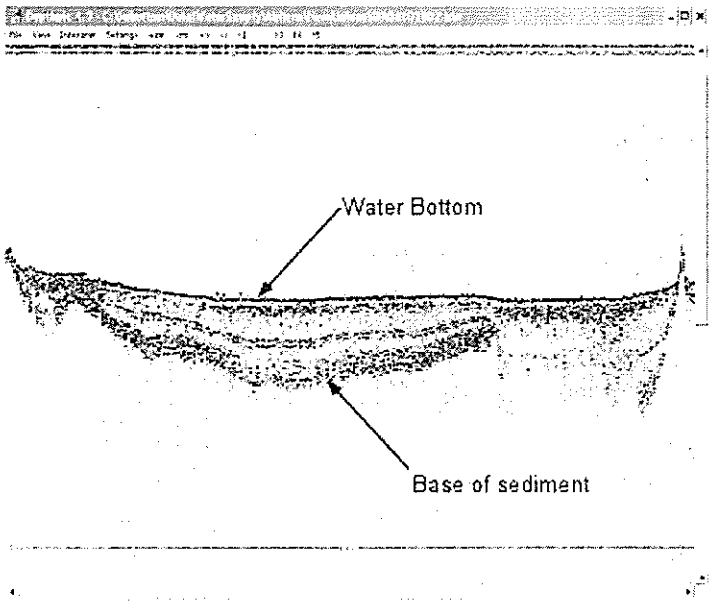


Figure B4-1. Example acoustic profile of reservoir bottom and sub-bottom. In the case shown, the 125 KHz profile penetrates to the base of the 1.2-m thick sediments deposited on the submerged floodplain on the left side of the profile. Lower frequency signals produced by the same system are used to penetrate thicker sediment in the submerged stream channel on the right of the profile.

To generate a water depth map the interpreted depths and horizontal positions for each profile are exported from *Depthpic* to an ASCII file of x, y, z values. These data are then merged with RTK GPS data from the dry portions of the reservoir, as described in the follow section. The merged x, y, z data files are read by a companion mapping program *Depthmap*, for contouring and volumetric analysis. *Depthmap* uses a different approach to mapping than conventional gridding. It is particularly well suited for data collected densely along widely spaced profiles, within irregularly shaped regions such as lakes and rivers. *Depthmap* initially generates a flat triangular mesh within the reservoir shoreline. The triangles sides are nominally the same size as the spacing between profile lines. The program then solves an optimization problem that deforms the surface to pass through the control data in a least-squares sense and to have

minimum curvature between data points. The water bottom and sediment thickness measurements are fit to separate surfaces and a root-mean-square (RMS) error between the data and surface computed for each surface. Volumes of water capacity and trapped sediment are then computed by numerical integration over the piecewise-triangular surfaces representing water depth and sediment thickness. The RMS error in the surface fit, times the surface area of the normal pool region of the reservoir is used as an indication of the uncertainty in volume estimates. The project goal is to determine the water storage capacity at normal pool elevation to within 5% error and the trapped sediment volume to within 10%, by this measure

B4.2.2 Analysis of land-based RTK GPS data

The measurements of the elevation of the dry parts of FRS using RTK GPS will be stored in digital files as x, y, z coordinates at discrete locations, with the elevation of the reservoir outlet works used as the reference for the z-coordinates. These data will be merged with acoustically measured water bottom elevation measurements from the water covered parts of the FRS and used to generate contour maps of the reservoir water depth and to compute water volume at the normal pool elevation. This will be done using the *Depthmap* program as described in the previous section.

Table B4-1. Summary of instrumentation, parameters, analytical methods and results

Instrument/ Equipment	Measured Parameters	Analytical Method	Analytical Result
YSI Model 30M meter	Water temperature and Conductivity	Del Grosso, 1974.	Speed of sound in water
Acoustic sub-bottom profiler	Digitally recorded acoustic profiles showing water column and sub-bottom	Interpretation via Depthpic, mapping via Depthmap	Water depth maps, water and sediment volumes.
Kinematic GPS	Ground elevation relative to outlet works in dry parts of reservoir	Mapping via Depthmap	Water depth maps, water and sediment volumes.
Electric vibracoring system (water)	Sediment cores	Visual inspection, computation of sediment water content	Sediment thickness, sediment dry weight density
Pneumatic vibracoring system (dry land)	Sediment cores	Visual inspection, computation of sediment water content	Sediment thickness, sediment dry weight density
Canberra gamma ray detector	^{137}Cs activity	Determination of first and peak activity	Location of 1954 and 1964 time lines in cores
Shimadzu TOC-V_{CSH}	Total Organic Carbon	Oxidative combustion and infrared analysis	Mass concentration of organic carbon in sediment samples
Lachat QuikChem 8500	Total N, Total P, NH_3-N, NO_2-N+$N0_3$-N	Flow injection Analysis	Mass concentration of common nutrients in sediment samples
Perkin-Elmer Elan DRC (II)	Concentration of Trace Metals	ICP-MS Spectrometry	Mass concentration of common trace metals in sediment samples
Hewlett-Packard 5880A	Concentration of Chlorinated Hydrocarbon Pesticides	CG/ECD	Mass concentration of common pesticides in sediment samples

This table summarizes the different instruments and equipment used in study, parameters measured with the instruments and equipment, analytical methods applied to those measurements, and the results produced from those analyses.

B4.3 Analytical methods for computation of sediment and contaminant mass

Once the average dry bulk density of the sediment, the total volume of the sediment, and the mass fraction of each contaminant species is known, the total mass of each trapped contaminant species can be computed. This is the mass of contaminant that would have remained in the surface water, if the reservoirs were not present. The total mass of each contaminant will computed using the formula

$$M_{species} = \rho_{db} V_s C_{species}, \quad \text{(B4-4)}$$

where $M_{species}$ is estimated total mass of the contaminant species in the reservoir, ρ_{db} is the dry bulk density of the sediment in the reservoir, as defined by Equation B4-1, V_s is the volume of the sediment determined from the sediment survey, and $C_{species}$ is the concentration of the contaminant species.

B4.4 Standards Traceability

Standards will be used in the calibration of the YSI temperature/conductivity meter and the Canberra gamma ray detector. All standards used will be traceable to certified reference materials. Documentation for each standard used will include information concerning the standard identification, starting materials, including concentration, amount used and lot number, date prepared, and expiration date, if any. Standards used by the CRASR and GERG laboratories are described in the appendices B through J.

B4.5 Failures in Measurement Systems and Corrective Actions

Failures in field measurement systems involve, but are not limited to such things as instrument malfunctions, failures in calibration, contamination, and quality control samples outside defined limits. In many cases, the field personnel will be able to correct the problem. If the problem is resolvable, then the personnel will document the problem in the field notes and complete the analysis. If the problem is not resolvable, then it is conveyed to the Field Supervisor, who will make the determination and notify the BUDG QAO. The BUDG Project Manager will include this information in the CAR and submit it with the Quarterly Progress Report to the TSSWCB Project Manager.

Section B5: Quality Control

The following quality control procedures will be followed to insure that errors resulting from instrument drift, instrument malfunction, sample contamination, or human error are detected. In each phase of the project, redundant measurements will be made and measurements of standards or known quantities will be repeated to insure data quality.

B5.1 Sediment surveying quality control

B5.1.1 Acoustic sub-bottom profiling quality control

The primary instrument used in the sediment surveys will be an acoustic sub-bottom profiling system manufactured by Specialty Devices, Inc. of Wylie, Texas (SDI). The SDI profiling unit includes transducers and associated electronics to produce and digitally sample acoustic signals, an integrated DGPS navigation system, and a controlling computer. The resulting digital data are manually interpreted during post-survey processing to produce water depth and sediment thickness measurements. The precision of the entire system will be determined by collecting multiple extra acoustic profiles that trend parallel to the reservoir thalweg and cross the normal survey profiles at approximately right angles. During post-processing these profiles are independently interpreted just like the regular profiles in the survey. A feature of the interpretation software then finds all the intersections between crossing lines and computes the RMS difference between the water depth and sediment thickness measurements at the intersection points. The resulting values are measures of the precision of the water depth and sediment thickness measurements. If all sub-systems of the survey system are working properly, including acoustics, navigation, and human interpretation, then measurements should be the same at locations the navigation system determines are the same points on the reservoir. RMS errors in excess of 10 cm are interpreted to indicate a problem has occurred in some part of the survey system. Tests of the accuracy of the acoustic and navigation subsystems are addressed in section B7.

B5.1.2 Navigation quality control

The DGPS navigation system is a critical part of the acoustic profiling, land surveying and coring operations. If the navigation system is not working properly, no useful data can be collected. For this reason, the Hypack software used to control the navigation function continuously monitors the number and quality of the signals received from the GPS satellites and the correction signal from the ground reference station. During operations, if the quality of these signals drops to the point that the instrument is receiving signals from fewer than the required number of satellites or the correction signal is lost, so that position accuracy of 1 m cannot be maintained, the unit flashes a warning on the computer monitor and operations will be stopped until the problem is corrected. In most cases, such problems can be corrected by relocating the antennas. In cases in which overhead obstructions, such as tree canopy, is obstructing the signal, nothing can be done. In these cases, the obstructed portions of the site cannot be surveyed. If

more than 10% of the area of the reservoir cannot be surveyed for this reason, one of the backup reservoirs will be selected to survey, as described in Section A7.6.

In addition to the automatic, continuous monitoring of the quality of the navigation data, two tests will be performed to manually check the accuracy and precision of the navigation. First, the accuracy of the navigation system will be tested prior to beginning the survey by stopping at USGS benchmark CA1092 on the way to the survey site and taking a DGPS fix on the mark. This test is done by recording the apparent position of the mark with the GPS antenna held on the mark for 1 minute and then computing the average location. The fix is then compared with the published geographic location of the mark. If the apparent position does not agree with the published position to within 1 m, the navigation system will be judged faulty and no survey work will be performed until the problem is corrected. Then at the survey site, the precision of the navigation system will be tested at least twice during the day. This test will be performed by recording the position of a fixed point on shore at the site in the morning prior to beginning the survey. The fix is then repeated at midday and at the end of the day. If the three fixes do not agree to within 1 m, the navigation system will be judged faulty, which would invalidate the data collected since the last successful test.

B5.2 ^{137}Cs analysis quality control

The second major instrument that will be used in the project is the Canberra gamma ray detector. The instrument reports the radioactivity of samples in units of pCi/g (picoCuries per gram) and assigns 95% confidence limits for each measurement. In cores in which the base of the core pre-dates the onset of ^{137}Cs deposition, there are two key samples: 1) the deepest sample in the core in which ^{137}Cs is detected, and 2) the sample that has the greatest concentration of ^{137}Cs. The correct interpretation of the ^{137}Cs results depends on the relative concentrations rather than their absolute values. Hence, precision is more important than accuracy. The repeatability of these key measurements is tested by repeating those measurements, plus the sample immediately below the deepest sample containing detectable amounts of ^{137}Cs and the sample that contains the second highest concentration of ^{137}Cs. Failure of the repeat measurements to fall within the 95% confidence interval of the initial measurement indicates a problem with the instrument. A change in the apparent first appearance or maximum concentration of ^{137}Cs between the two runs indicates an ambiguous result. To resolve ambiguous results, the samples will be run again at twice the count time (160,000 s). The test of the accuracy of the gamma ray detector is described in section B7.

B5.3 CRASR Laboratory Measurement Quality Control Requirements and Acceptability Criteria

Detailed laboratory QC requirements are contained within each individual method and laboratory quality assurance manuals (QAMs). The minimum requirements that the CRASR Laboratory abides by are stated below.

Lab QC samples are prepared and analyzed in batches, which are defined as follows:

Batches are environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of 1-20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) that are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

Laboratory splits - Laboratory duplicates are used to assess precision. A laboratory duplicate is prepared by splitting aliquots of a single sample (or a matrix spike or a laboratory control standard) in the laboratory. Both samples are carried through the entire preparation and analytical process. Laboratory duplicates are run at a rate of one per preparatory (if applicable) and analytical batch. Acceptability criteria are outlined in Table A7-1.

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:

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

Laboratory Control Standard (LCS)/Laboratory Control Standard Duplicate (LCSD) – LCS/LCSD pairs are analyte-free water samples spiked with the analyte of interest prepared from standardized reference material. The LCS/LCSD pairs are generally spiked into laboratory pure water at a level less than or equal to the mid-point of the calibration curve for each analyte. They are carried through the complete preparation and analytical process. The LCS/LCSD pairs are used to document the bias of the method due to the analytical process. Bias can be assessed by measuring the percent recovery of LCSs and LCSDs, and precision can be assessed by comparing the results of LCS/LCSD pairs. LCS/LCSD pairs are run at a rate of one each per preparatory (if applicable) and analytical batch. Precision and bias criteria for LCS/LCSD pairs are specified in Table A7-1. Laboratory-specific control limits and charts are calculated and maintained by laboratory staff on a periodic basis.

Bias of LCSs and LCSDs is expressed by percent recovery (%R) where SR is the observed spiked sample concentration, and SA is the spike added:

$$\%R = SR / SA * 100$$

The mean bias of LCS/LCSD pairs is expressed by $\%R_{mean}$, where $\%R_{LCS}$ is the percent recovery of the LCS and $\%R_{LCSD}$ is the percent recovery of the LCSD:

$$\%R_{mean} = (\%R_{LCS} + \%R_{LCSD}) / 2$$

Precision between LCS/LCSD pairs is expressed by relative percent difference (RPD). For LCS/LCSD results, X_1 and X_2, the RPD is calculated from the following equation:

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

Matrix spikes (MS) – A matrix spike is an aliquot of sample spiked with a known concentration of the analyte of interest. Percent recovery of the known concentration of added analyte is used to assess accuracy of the analytical process. The spiking occurs prior to sample preparation and analysis. Matrix spike samples are routinely prepared and analyzed at a rate of 10% of samples processed or one per preparatory (if applicable) and analytical batch whichever is greater. The MS is spiked at a level less than or equal to the midpoint of the calibration or analysis range for each analyte. The MS is used to document the accuracy of a method due to sample matrix and not to control the analytical process. Percent Recovery (%R) is defined as 100 times the observed concentration, minus the sample concentration, divided by the true concentration of the spike. MS recoveries are indicative of matrix-specific biases and are plotted on control charts maintained by the laboratory. Measurement performance specifications for matrix spikes are not specified in this document, and MS data should be evaluated on a case-by-case basis.

The formula used to calculate percent recovery, where %R is percent recovery; SSR is the observed spiked sample concentration; SR is the sample concentration; and, SA is the spike added, is:

$$\%R = (SSR - SR) / SA * 100$$

AWRL/Reporting Limit Verification – The laboratory's reporting limit will be at or below the AWRL. To demonstrate ongoing ability to recover at the reporting limit, the laboratory will analyze a calibration standard (if applicable) at or below the reporting limit on each day samples are analyzed. Two acceptance criteria will be met or corrective action will be implemented. First, calibrations including the standard at the reporting limit will meet the calibration requirements of the analytical method. Second, the instrument response (e.g., absorbency, peak area, etc.) for the standard at the reporting limit will be treated as a response for a sample by use of the calibration equation (e.g., regression curve, etc.) in calculating an apparent concentration of the standard. The calculated and reference concentrations for the standard will then be used to calculate percent recovery (%R) at the reporting limit using the equation:

$$\%R = CR / SA * 100$$

where CR is the calculated result and SA is the actual or reference concentration for the standard. Recoveries must be within 75-125% of the reference concentration.

When daily calibration is not required, or a method does not use a calibration curve to calculate results, the laboratory will analyze a check standard at the reporting limit on each day samples are analyzed. The check standard does not have to be taken through sample preparation, but must be recovered within 75-125% of the reference concentration for the standard. The percent recovery of the check standard is calculated using the following equation in which %R is percent recovery, SR is the sample result, and SA is the reference concentration for the check standard:

$$\%R = SR / SA * 100$$

If the calibration (when applicable) or the recovery of the calibration or control standard is not acceptable, corrective actions (e.g., re-calibration) will be taken to meet the specifications before proceeding with analyses of samples.

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 (if applicable) and analytical batch. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination from the analytical process. The analysis of method blanks should yield values less than the laboratory's reporting limit. For very high-level analyses, blank value should be less then 5% of the lowest value of the preparatory (if applicable) and analytical batch or corrective action will be implemented.

B5.4 GERG Laboratory Measurement Quality Control Requirements and Acceptability Criteria

The quality control methods followed by the GERG Laboratory are described for each analysis type they will perform in Appendices G, H, I, and J.

B5.5 Failures in Quality Control and Corrective Action

Sampling QC excursions will be evaluated by the BUDG Project Manager, in consultation with the BUDG QAO. In that differences in sample results are used to assess the entire sampling process, including environmental variability, the arbitrary rejection of results based on pre-determined limits is not practical. Therefore, the professional judgment of the BUDG Project Manager and QAO will be relied upon in evaluating results. Rejecting sample results based on wide variability is a possibility. Method blanks for trace elements and trace organics will be scrutinized closely. Corrective action will involve identification of the cause of the failure where possible. Response actions will typically include re-analysis of questionable samples.

Section B6: Instrument/Equipment Testing, Inspection, and Maintenance

The instruments that will be used in this project were all inspected and tested upon receipt and are assured appropriate for use by routine calibration procedures described below.

The following is a list of instrumentation and equipment to be used in the project.

1. YSI temperature/conductivity meter, Model 30M, or similar meter.
2. Specialty Devices, Five Frequency Acoustic Sub-bottom profiler.
3. Specialty Devices, Kinematic GPS positing system.
4. Specialty Devices, Vibracoring system.
5. Canberra Gamma Ray Detector, Model Number GC2520.
6. Shimadzu TOC-VCSH Carbon Analyzer.
7. Lachat Quickchem 8500 Flow Injection Autoanalyzer.
8. Perkin-Elmer Elan DRC (II) ICP Mass Spectrometer.
9. Hewlett-Packard 5880A CG/ECD.

To minimize downtime of all field measurement systems, sampling equipment, and laboratory equipment, will be maintained in a working condition. All field and laboratory equipment will be tested, maintained, and inspected in accordance with manufacturer's instructions. Maintenance and inspection logs will be kept on each piece of laboratory equipment. General maintenance checklists will be filled out for field sampling equipment, by the field technician.

Failures in any testing, inspections, or calibration of equipment will result in a CAR and resolution of the situation will be reported to the TSSWCB in the quarterly report. CARs will be maintained by the BUDG Project Manager.

Section B7: Instrument/Equipment Calibration and Frequency

B7.1 Calibration of the navigation equipment

The DGPS and RTK GPS navigation equipment used in the project must be tested, but does not require operator calibration. These instruments measure geographic position by triangulation relative to satellites at precisely known locations by measuring the transit time of radio signals from the satellites to the units on the ground. The raw positions are then corrected in real time for variations in the speed of the radio signals through the atmosphere by applying a correction signal generated by one or more similar units at fixed, known locations. In this sense, DGPS and RTK GPS systems are continuously self-calibrating. Verification that the systems are working properly will be done in two ways each field day as described in Section 5.1.2.

B7.2 Calibration of the YSI temperature/conductivity meter

A YSI temperature/conductivity meter will be used in this project to measure the temperature and electrical conductivity of reservoir water from which the speed of sound can be calculated. The speed of sound in the reservoir water is used in calibration of the acoustic profiling system as described below. The YSI meter measures temperature indirectly by measuring the resistance of a semiconductor device, a thermistor, which is designed to have a resistance that is highly sensitive to temperature. The relationship between the resistivity of the thermistor and temperature is relative stable, but its calibration is tested in the lab before taking the instrument to the field, by placing the sensor in an ice/distilled water mixture and in boiling distilled water.

The YSI meter measures the conductivity of water by measuring the voltage between two electrodes driven by a known current. This measurement is less stable than the temperature measurement made by the meter. Therefore, calibration is carried out before each field day, by placing the sensor in standard solutions of known electrical conductivity. Two standard solutions are used, one with a lower conductivity than that of common surface waters and the other will a higher conductivity than that common surface waters. Quality control and calibration procedures for YSI meters are described in Appendix A.

B7.3 Calibration of the SDI acoustic sub-bottom profiler

The acoustic profiling instrument directly measures the round-trip travel time of acoustic signals from the transducer array to the bottom or sub-bottom and back to the transducer array. The main aspects of this measurement that require calibration is the speed of sound in water and the delay between the onset of the voltage rise applied to the transducer to produce the acoustic pulse and the time at which the first acoustic sample is recorded. The speed of sound in the water can be calculated to within a small fraction of a percent using an empirical relationship between speed of sound in water and the water temperature and salinity (Del Grosso, 1974). This is done by measuring the water temperature and electrical conductivity within the reservoir on the day of

the survey by collecting a vertical profile through the water column using the calibrated YSI temperature/conductivity meter described in the previous section. Conductivity is then related to salinity using a second empirical relationship (Poisson, 1982). The speed of sound in water varies less than 2% from 20 to 30 °C (1482.8 to 1509.5 m/s) for typical Texas surface waters. Because water in shallow FRS tends to be well stirred by winds, this correction accounts for nearly all the variation in the speed of sound in water.

To measure the time it takes acoustic signals to travel through the water, reflected from the bottom, and return to the transducer, two things have to happen. The transducer must produce the sound pulse and the acoustic returns must be recorded. The two must be closely synchronized to accurately measure the signal transit time. The delay times and accuracy with which the system measures water depth are tested by what is referred to as a "bar check". The bar check is conducted by suspending a distinct acoustic target at a known depth in the water directly below the transducer array. For bar checks, BUDG uses a rectangular aluminum plate suspended 2 to 5 m below the acoustic array, depending on water depth. A short record is acquired, using each signal frequency. If the correct water velocity is used and the correct delays are set for each transducer, the target should appear at the correct depth on the displays for each frequency. If the target appears at the wrong depth by the same amount on the records for all of the transducers, the speed of sound is likely in error. If the target appears at different depths at different signal frequencies, the delays are set wrong. In these cases, the speed of sound and/or the transducer delay settings are adjusted until all frequencies read the correct depth. Then to re-check the settings, the target is moved to a different depth and the process is repeated. The correct settings result in correct depth readings at all depths on all signal frequencies. The bar check was done in the factory before the instrument was shipped and the settings generally do not change rapidly with time. However, the characteristics of acoustic transducers do change slowly over time as they age. Hence, the bar check is repeated at the beginning of each survey to ensure the correct speed of sound is being used and that the instrument is working properly.

B7.4 Calibration of the Canberra Gamma Ray Detector

The concentration of ^{137}Cs in sediment samples is determined by placing a 25 g sample of powered and sieved sediment in a 50x9 mm Petri dish and placing the dish in a lead-shielded chamber containing a Germanium detector. The gamma rays emitted by the sample that fall within a Gaussian window about 661.65 KeV are then counted for 80,000 s (22.2 hr). In addition to the concentration of ^{137}Cs in the sample, the resulting count is influenced by the sensitivity of the gamma ray detector, the geometry of the detector, the geometry of the sample, the density of the sample and its self-shielding properties, and background radiation. The background radiation occurs as a result of cosmic radiation that makes it through the lead shielding, radioactive materials within the shielding, and any contaminants that may have inadvertently found their way into the sample chamber.

To quantitatively interpret the resulting count in terms of the concentration of ^{137}Cs, the instrument must be calibrated and the background radiation must be determined. To calibrate the instrument, a standard sample with a known ^{137}Cs activity is analyzed. The standard was prepared for BUDG by Isotope Products Laboratories of Valencia, CA, and is designated Source

Number 1120-54. This is a multi-isotope source with a total activity of 0.8986 μCi. The active ingredients in the source are contained in an epoxy-impregnated powder of the same density as the average density of the typical dried sediment samples. To prepare the standard, material of known ^{137}Cs activity was mixed with a filler material, which matches the average density of powdered siliceous sediment. This mixture was then placed in an example of the Petri dishes BUDG uses as containers and sealed. To calibrate the instrument, the standard sample is placed in the detector chamber and counted for 80,000 s, in the same way sediment samples are counted. The resulting count, along with the number of days that had passed since the manufacture date of the standard are used to compute a geometric correction factor that is applied to observed counts in the ^{137}Cs analysis process. The background radiation level is determined by placing a sealed, empty Petri dish in the detector and counting the background radiation for 80,000 s. The resulting count was used to compute a background correction that is also applied to the observed counts. To test for the proper operation of the instrument and any changes that may have occurred in the system, the calibration and background tests are re-run, accounting for the increased time that has past since the manufacture date of the standard. These tests are done before and after running samples for a given project. If the results of the repeat calibration test fail to fall within the 95% confidence interval of the original calibration tests, they are repeated. Multiple failures to match the initial tests would indicate contamination of the instrument or instrument malfunction, requiring maintenance and the sample runs made since the last successful test would be invalidated.

B7.5 Calibration of Shimadzu Carbon Analyzer

For TOC, the Shimadzu Carbon Analyzer is calibrated with five standards (1, 5, 10, 20, and 30 mg/L). This calibration is stored and used repeatedly. The instrument is recalibrated when recoveries of known sample concentrations fall below 90%. Both calibrations require an r-value of at least 0.99900.

B7.6 Calibration of Lachat Quickchem

The Lachat Quickchem is calibrated using an eight point calibration (0, 5, 10, 25, 50, 100, 250, 500, and 1000 ug/L) which is generated for every run for dissolved (NO_2+NO_3, NH_3) and total nutrients (N and P). Dissolved nutrients can be run individually or in any combination. Total nutrients are run separately.

B7.7 Calibration of ICP MS

A 4-point calibration curve, using background correction, is used in this procedure. The ICP-MS is linear over a wide concentration range. The ICP-MS software uses a weighted linear least-square fit for low-level determinations which permits low concentrations to have more of an impact on the fit of calibration line. The correlation coefficient (r) should be $\geq$0.9950 for each analyte in the calibration curve. The absolute value of the concentration for an element in the calibration blank should be less than the ML or CRDL for each element in question. The RSD for three replicates at 10 ppb level should be $\leq$1% and at 1 ppb the RSD should be $\leq$5% for most elements. Significantly worse precision may be due to inadequate uptake time, exhausting the

standard, sample introduction problems, solution chemistry, or wavelength alignment. The initial calibration data together with the printout of the Accepted Values screen should be stored in the appropriate ICP-MS calibration file. A blank (ICB) is run after each calibration and/or at the beginning of each analytical set. If the absolute calculated value for any analyte is higher than the Contract Required Detection Limit (CRDL) or the ML, corrective action should be taken. Corrective action may include a calibration update, instrumental maintenance and/or recalibration. A blank (CCB) is run after each 10 samples or after each 2 hours (whichever is sooner) and at the completion of each analytical set. If the absolute calculated value for any analyte is higher than the CRDL or the ML, corrective action should be taken. Corrective action may include terminating analysis, a calibration update, instrument maintenance and/or recalibration.

B7.8 Calibration of GC/EDD

Pesticide/PCB calibration is done as part of the analytical run. The four calibration mixtures are interspersed with actual samples during the GC/ECD analyses. The calibration curve is then based on these four standards. If the calibration curve has an r^2 of 0.995 or higher for all analytes present in the samples it is accepted, if not the calibration standards as well as all the samples must be reanalyzed by GC/ECD. This procedure is superior to the procedure where the instrument is initially calibrated at four points and then mid-level standards are run during the analytical run. This latter calibration only insures that mid-level samples remain in calibration. Since the ECD detector is nonlinear, a one-point check on its calibration is not as rigorous as calibration during the GC/ECD run.

Section B8: Inspection/Acceptance for Supplies and Consumables

All new batches of field and laboratory supplies will be inspected and tested before use to ensure that they are adequate and not contaminated. The raw stock aluminum and stainless steel tubing used in coring is cut to length, core catching devices are riveted to the inside bottom of the tubes, and the tubes and caps are ethanol and acid washed and dried.

standard, sample introduction problems, solution chemistry, or wavelength alignment. The initial calibration data together with the printout of the Accepted Values screen should be stored in the appropriate ICP-MS calibration file. A blank (ICB) is run after each calibration and/or at the beginning of each analytical set. If the absolute calculated value for any analyte is higher than the Contract Required Detection Limit (CRDL) or the ML, corrective action should be taken. Corrective action may include a calibration update, instrumental maintenance and/or recalibration. A blank (CCB) is run after each 10 samples or after each 2 hours (whichever is sooner) and at the completion of each analytical set. If the absolute calculated value for any analyte is higher than the CRDL or the ML, corrective action should be taken. Corrective action may include terminating analysis, a calibration update, instrument maintenance and/or recalibration.

B7.8 Calibration of GC/EDD

Pesticide/PCB calibration is done as part of the analytical run. The four calibration mixtures are interspersed with actual samples during the GC/ECD analyses. The calibration curve is then based on these four standards. If the calibration curve has an r^2 of 0.995 or higher for all analytes present in the samples it is accepted, if not the calibration standards as well as all the samples must be reanalyzed by GC/ECD. This procedure is superior to the procedure where the instrument is initially calibrated at four points and then mid-level standards are run during the analytical run. This latter calibration only insures that mid-level samples remain in calibration. Since the ECD detector is nonlinear, a one-point check on its calibration is not as rigorous as calibration during the GC/ECD run.

Section B9: Non-Direct Measurements

The horizontal control survey will be based on an existing monument with published National Geodetic Survey (NGS) position and elevation (NGS, 2006). Position verification of the GPS will be performed using monument CA1092, which is located 8 miles south of Brady, Texas on Ranch Road 734. Lake level elevations will be determined relative to the reservoir outlet elevation on each day of surveying. The outlet works for each reservoir surveyed will be used as the local elevation datum for that survey.

Section B10: Data Management

B10.1 Field Collection and Management of Digital Data

During sediment surveys, the sub-bottom acoustic profiling instrument is the primary data logging tool. The instrument logs the time of day each reading is collected, an initial estimate of the water depth, instrument settings, geographic location, and the acoustic record itself all to its hard drive. These records are collected approximately 4 times per second as the survey vessel travels along the survey lines. These data are recorded in an open binary format maintained by Specialty Devices, Inc. Similar geographic and elevation records are recorded during land surveying, without the acoustic recordings. All recordings are downloaded to USB Flash memory drives at the end of each field day as a backup, but also retained on the field instrument hard drives until the final archive of the data is complete. Prior to processing, all digital data are compiled under a single directory on the processing work stations, labeled "SDIBinFiles", for each reservoir surveyed.

During coring operations, the geographic position of each core site is recorded by the Hypack navigation software as a navigation target. All the targets generated during a survey are recorded in an ASCII file with the file extension "*.trg" by Hypack. This file, along with Hypack setup files that define the reservoir shore and planned profile lines are all archived along with the field acoustic data. For FRS the total size of all field record files is typically on the order of 1 gigabit and can be archived on a single DVD.

During post-survey processing, numerous derivative files are generated. For each acoustic profile a separate file is generated for each manually interpreted survey that records the type of surface (depth or isopach thickness), the surface number recorded, the units in which the measurements are made, the speed of sound used to convert from signal travel time to distance, the measured transducer depth in the water, the measured water surface elevation, a flag that indicates if valid navigation data were recorded, and another flag for the mode in which the trace positions are recorded in the file (X-Y, Latitude-Longitude, or distance along profile). Then for each acoustic trace in the file, there is an entry for the position of the trace, the manually interpreted depth or thickness value and the trace number. These files are stored with the file type extension "*.pic" and can be re-read by the interpretation program *Depthpic* and re-displayed over the acoustic data to check or edit interpretations. This is the primary tool used to check the quality and consistency of interpretations made by different interpreters. The "*.pic" files are written in ASCII format that can be read by any text editing program.

In addition to "*.pic" files, separate files are generated for each interpreted surface that list the geographic location and interpreted depth or layer thickness at each trace location. These files are written to with file extensions "*.xyz", in ASCII format, which can be read by virtually all mapping and GIS programs.

Once all the profiles have been interpreted the "*.xyz" files are read into a companion program *Depthmap* to generate the surface maps and perform the volumetric calculations. *Depthmap*

generates contour maps that can be saved as "*.bmp" images and volumetric reports stored in ASCII format with the file extension "*.vol". In addition the geographic location, elevation, depth or thickness of each corner point in the triangular surface model is written to an ASCII file with the extension "*.map". All of the derivative data files generated during post-survey processing for each reservoir are collected into separate sub-directories and labeled by file type and archived on a single CD. Two copies of all raw and derivative data are made and stored in separate locations.

B10.2 Auxiliary field notes and data

In addition to electronically recorded data, some field data are manually recorded. These include the elevation difference between the outlet works and the water surface, water temperature, electrical conductivity and depth measurements, and manually recorded geographic positions for the outlet works, the core locations, and navigation system check locations. All of these field notes are recorded in bound surveyor's notebooks with 50% rag paper that has been treated with water resisting surface sizing. Entries in the notebooks are identified by reservoir name and the date of the survey. The notebooks for all surveys done by BUDG are consecutively numbered and kept permanently.

B10.3 Core sub-sampling notes and data

Prior to sub-sampling longitudinally sliced cores are optically scanned and the images are stored in "*.bmp" format. Information generated during the core sub-sampling process is initially recorded on the Core Sub-sampling Form (Appendix M). Entries are labeled by reservoir name, core number and letter, and the date of the sub-sampling operation. Entries for each sub-sample include the sample number, the weight of the container in which the sample is placed, the weight of the sample plus container in its wet condition, the weight of the sample plus container after it is dry, the weight of a measured volume of a bulk density sample, the penetration resistance of the sample, and the physical appearance of the sample. In particular, apparent texture, color, and the presence of plant fragments or intact roots are noted. The total core length and an initial estimate of the depth to the pre-impoundment surface, if it is present in the core are also noted. Once the sub-sampling process is complete, the lab notes for each core are transcribed to an Excel file. New entries in the file are generated for sample water content by weight, bulk density, dry and bulk density. The Excel files for each core are archived along with the derivative sediment survey files for each reservoir.

B10.4 ^{137}Cs analysis files

The Canberra digital spectrum analyzer that performs the ^{137}Cs analysis is controlled by a Canberra computer program called Genie™. This program also automatically locates spectral peaks, identifies the likely isotope associated with each peak, computes the area of each peak, applies the various corrections to the areas, and computes activities associated with each identified isotope in the sample. This information, along with the time, date and duration of the count, are recorded in an ASCII file generated for each sample run. The files for each sample run are stored in separate subdirectories for each core and archived in two places. BUDG

maintains a master archive of all sample runs generated by BUDG since its inception and also stores copies of the directories for each core with the derivative survey results associated with each reservoir.

B10.5 CRASR Laboratory Analysis

The analysis of organic carbon and nutrient concentrations in core samples will be performed by the CRASR Laboratory. The samples for the entire project will be run in separate batches for each of the three extraction methods used. Laboratory personnel fill out a form for each sample batch they run (Appendix O).

B10.6 GERG Laboratory Analysis

The analysis of trace metals and pesticides in core samples will be performed by the GERG Laboratory. Laboratory personnel fill out forms SD-191 to document the sediment digestion procedure (Appendix G, Figure 1) and an inorganic analysis form (Append G, Figure 2) for each batch of samples analyzed for trace metals.

Section C1: Assessments and Response Actions

C1.1 Field and laboratory assessments

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 being employed and being employed properly. This verification will be provided through a field and laboratory performance audit performed by the TSSWCB QAO or designee. 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 sites will be addressed by the project participants and followed up with a CAR. Follow-up observations will occur when discrepancies are noted, as possible within the budget and duration of this project.

All laboratory analyses will have the precision and accuracy of data determined on the particular day that the data were generated. The specific requirements are presented in Section B5.

Table C1-1 Assessment activities

Assessment Activity	Approximate Schedule	Responsible Party	Scope	Response Requirements
Status Monitoring Oversight, etc.	Continuous	BUDG, CRASR, GERG	Monitoring of the project status and records to ensure requirements are being fulfilled. Monitoring and review of contract laboratory performance and data quality.	BUDG will report to TSSWCB PM via quarterly report.
Laboratory Inspections	Once during life of project	TSSWCB QAO	Analytical and QC procedures employed at the laboratory.	BUDG has 30 days to respond in writing to the TSSWCB QAO to address corrective actions
Monitoring Systems Audit	Once during life of project	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.	BUDG has 30 days to respond in writing to the TSSWCB QAO to address corrective actions

C1.2 Audits

The BUDG Project Leader and the Field Supervisor are 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 Project Leader and Field Supervisor 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 BUDG personnel and will note activities conducted in connection with the sediment survey and coring program, items or areas identified as potential problems, and any variations or supplements to the QAPP. Corrective action report forms will be used when necessary (Appendix K). CARs that result in any 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 and laboratory measurements made during 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. CARs will be filled out to document the problems and the remedial action taken.

Copies of all CARs for this project will also be included with the project final report. 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 BUDG Project Leader, Field Supervisor, and QAO.

Section D1: Data Review, Verification and Validation

For the purposes of this document, verification means the processes taken to determine compliance of data with project requirements, including documentation and technical criteria. Validation means those processes taken independently of the data-generation processes to determine the usability of verified data for its intended use(s). Integrity means the processes taken to assure that no falsified data will be reported.

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 DQOs outlined in Section A7. 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. The BUDG Field Supervisor is responsible for ensuring that any pertinent field data is properly reviewed, verified, and submitted in the required format for the project database. The CRASR and GERG laboratory directors 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 Data Supervisor in the required format for the project database.

The laboratory directors shall be responsible for reviewing raw data produced. The Data Supervisor shall be responsible for reviewing raw data produced by the laboratory. The Project Leader shall check calculations to verify that data are entered into the database correctly and be responsible for internal lab error corrections. CARs will be initiated in cases where invalid or incorrect data have been detected.

Representativeness and comparability of data, while unique to each individual collection site, is the responsibility of the Project Leader. 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 analyses will be the responsibility of the Laboratory Director.

The Project Leader 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.

Section D2: Verification and Validation 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. A Data Review Checklist is included in Appendix L. 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 (Table D2-1). The field and laboratory tasks ensure the verification of raw data, and electronically generated data.

Table D2-1: Laboratory Sample Analysis Verification Form

Data to be Verified	Laboratory Task	Database (or Project Team's Data Manager) Task
Sample documentation complete; samples labeled, sites identified	√	
Standards and reagents traceable	√	
Chain of custody complete/acceptable	√	
Sample preservation and handling acceptable	√	
Holding times not exceeded	√	
Field documentation complete	√	
Nonconforming activities documented		√
Outliers confirmed and documented; reasonableness check performed		√
Dates formatted correctly		√
Depth reported correctly		√
Valid Parameter codes		√
Absence of transcription error confirmed		√
Absence of electronic submittal errors confirmed		√
Sampling and analytical data gaps checked (e.g., all samples for which data are reported are present)		√
Verified data log submitted		√
10% of data manually reviewed		√
Instrument calibration data complete	√	
QC samples analyzed at required frequency	√	√
Analytical sensitivity (MALs/AWRLs) consistent with QAPP	√	√
Results, calculations, transcriptions checked	√	
Laboratory bench-level review performed	√	
Collection, preparation, and analysis consistent with SOPs and QAPP		√

Excel will be used for general spreadsheet computation and laboratory control charting of quality control parameters. The Baylor University laboratory will employ various data handling software on IBM-compatible personal computer stations for data on the analyzed parameters.

The Project Leader is responsible for review of calculations and charts made by these programs. The Project Leader, Field Supervisor and CRASR QAO, as appropriate, 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.

The BUDG Project Leader 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 reservoir individually, as well as all sites collectively, for their ability to meet the DQOs of the project and the informational needs of water quality agency decision-makers. Statistical analysis and calculations will also be reviewed and verified as accurate. These summaries will be included in the final report.

Section D3: Reconciliation with User Requirements

Data produced in this project will be analyzed and reconciled with project data quality requirements. Data meeting project requirements will be used by the TSSWCB to determine reductions in NPS loadings, specifically those associated with the repair of FRS in McCulloch County and to aid in targeting locations where further reduction efforts are needed. Data that do not meet project requirements will not be used.

D3.1 Evaluate uncertainty and limitations on data.

The uncertainty and limitations of the results of this study are dependent on site conditions that cannot be predicted before the surveys have been preformed. During the project, estimates will be made for the uncertainty in the volume of sediment within each surveyed reservoir, the dry bulk density of the sediment in the reservoirs, and the concentration of contaminant species in the sediments. In the final analysis, these contributions to the overall error will be combined to produce error bounds for each quantity of interest of the study.

Of the factors that contribute to error in all the results produced in this study, error in the total sediment volume will likely be the most important. If the FRS are filled to near the normal pool elevation and the water depth is greater than the sediment thickness over most of the reservoir, the sediment thickness can be measured directly by acoustical measures. In these cases, the sediment volume can be determined within 10%, provided the survey coverage of the reservoir satisfies the completeness condition. If a significant area of the normal pool is dry during the survey or the water depth in the reservoir is such that the water depth is less than the sediment thickness, then the sediment volume must be estimated from the apparent change in water storage volume at the normal pool level. The accuracy of these results is dependent on the accuracy of the original volume estimates by NCRS. In the 23 FRS surveys previously conducted by BUDG to date (Section A6.3), a comparison of sediment volumes determined by direct measure of sediment thickness versus the apparent chance in water storage volume indicates the error in the latter approach can vary from less than 1% to over 50%. As part of the analysis of the survey data, BUDG will estimate the bounds on the error in sediment volume for each FRS surveyed and how that error level influences all dependent results.

References

Bennett, S. J., Rhoton, F. E., and Dunbar, J. A., 2005. Texture, spatial distribution, and rate of reservoir sedimentation within a highly erosive, cultivated watershed: Grenada Lake, Mississippi, Water Resources Research, v. 41, p. 1-11.

Del Grosso, V. A., 1974. New equation for the speed of sound in natural waters (with comparisons to other equations), Journal of Acoustical Society of America, vol. 56, p. 1084-1091.

Dendy, F. E., 1968. Sedimentation in the nation's reservoirs. Journal of Soil and Water Conservation, 23, 135-137.

Dendy, F. E., 1974. Sediment trap efficiency of small reservoirs, Transactions of the ASAE, v. 17, p. 898-908.

Dendy, F. E., 1982. Distribution of sediment deposits in small reservoirs, Transactions of the ASAE, v. 25, p. 100-104.

Dunbar, J.A., P.M. Allen, and S.J. Bennett, 2001, Acoustic imaging of sediment impounded by a USDA-NRCS flood control dam, Oklahoma. USDA-ARS National Sedimentation Laboratory Research Report No. 22, 54 pp.

Dunbar, J.A., Allen, P.M., Higley, P.H., 1999, Multifrequency Acoustic Profiling for Water Reservoir Sedimentation Studies. Journal of Sedimentary Research: Vol. 69, no. 2 pp. 521-27.

EPA, 2001. Method for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual, EPA-823-B-002, U. S. Environmental Protection Agency, Washington, DC.

Greiner, J. H., 1982. Erosion and sedimentation by water in Texas, average annual rates estimated in 1979, Report 268, Texas Department of Water Resources, Austin Texas, 250 p.

Lanesky, D.E., B.W. Logan, R.G. Brown, and A.C. Hine, 1979. A new approach to portable vibracoring underwater and on land. Journal of Sedimentary Petrology, 49, 654-657.

Neitsch, S. L., J. G. Arnold, J. R. Kiniry, R. Srinivasan, and J. R. Williams, 2005, Soil and Water Assessment Tool theoretical documentation, version 2005, Temple, Texas, Grassland, Soil and Water research Laboratory, Agricultural Research Service, Available at: www.brc.tamus.edu/swat/doc.html.Accessed_1_November_2006.

Poisson, A., 1982. Conductivity salinity temperature relationships of diluted and concentrated standard sea-water, Marine Geodesy, v. 5, p. 359-361.

USACE, 2001. Hydrographic Surveying, EM 1110-2-1003, Jan. 2001, United States Army Corps of Engineers, Washington, DC.

USACE, 1989. Sedimentation Investigations in Rivers and Reservoirs, EM 1110-2-1400, Dec. 1989, United States Army Corps of Engineers, Washington, DC.

Van Metre, P. C., J. T. Wilson, G. R. Hardwell, M. O. Gary, F. T. Heitmuller, and B. J. Mahler, 2003, Occurrence, Trends, and Sources in Particle-Associated Contaminants in Selected Streams and Lakes in Forth Worth, Texas, U.S. Geological Survey, Water-Resources Investigations Report 03-4169.

Van Metre, P. C., J. T. Wilson, C. C. Fuller, E. Callender, and B. J. Mahler, 2004, Collection, Analysis, and Age-Dating of Sediment Cores From 56 U.S. Lakes and Reservoirs Sampled by the U.S. Geology Survey, 1992-2001, Scientific Investigations Report 2004-5184, U.S. Department of the Interior, U.S. Geological Survey, Reston Virginia.

Ott, L. 1984. An Introduction to Statistical Methods and Data Analysis, 2nd Edition. Duxbury Press, Boston., Massachusetts.

SCS, United States Department of Agriculture Soil Conservation Service. 1985. National Engineering Handbook, Section 4 - Hydrology. Engineering Division. Washington, D.C. Report No. SCS/ENG/NEH-4-2.

Smith, D.G., 1984. Vibracoring fluvial and deltaic sediments: Tips on improving penetration and recovery. Journal of Sedimentary Petrology, 54, 660-663.

TCEQ. September 2003. Surface Water Quality Monitoring Procedures Volume 1: Physical and Chemical Monitoring Methods for Water, Sediment and Tissue. Austin, Texas.

Ritchie, J.C., 1998, ^{137}Cs use in estimating soil erosion: 30 years of research, p. 5-12, In: International Atomic Energy Agency (ed), Use of ^{137}Cs in the Study of Soil Erosion and Sedimentation, IAEA-TECDOC-1028, Vienna, Austria.

Richie, J. C., C. M. Cooper, and Jr. McHenry, 1986, Sediment accumulation rates in lakes and reservoirs in the Mississippi River valley, pp. 1357-1365, In: S. Y. Wang, H. W. Shen, and L.Z. Ding (eds.) *River Sedimentation*, Vol. III, University of Mississippi, Oxford, MS.

Appendix A

CENTER FOR RESERVOIR AND AQUATIC SYSTEMS RESEARCH (CRASR) STANDARD OPERATING PROCEDURE # 1.0 - Field Determination of temperature, dissolved oxygen, pH, conductivity, turbidity and chlorophyll-a in water utilizing YSI multiprobe instruments Revision 0 Adopted April 1, 2006

1. Method description

Multiparameter data sondes measure field water quality parameters through the use of sensors that are located on multiple probes. Readings are commonly taken either instantaneously, or sondes are deployed in a logging mode for unattended monitoring. Temperature, dissolved oxygen, pH and conductivity multiprobe technology has been in use for many years and this data is accepted by both federal (USEPA) and state (TCEQ) water quality monitoring agencies. These parameters are measured by both YSI sonde models currently used by CRASR—the 600XLM and the 6600 extended deployment system (EDS). The inclusion of turbidity and Chl-a sensors on multiprobe instruments is relatively recent, and they are only present on the 6600 EDS sondes. These data are commonly collected for use in special studies, but it is unclear at present if it routinely meets the precision limits required by federal and state water quality monitoring agencies.

2. Additional resources—in addition to this SOP, users of CRASR's YSI multiprobe instruments should familiarize themselves with the YSI user's manual and with the TCEQ's surface water quality procedures manual. Electronic copies of both are maintained on the laboratory computer, and hard copies are maintained in conjunction with CRASR's YSI calibration and maintenance logbook.

2. Equipment and supplies

2.1. YSI Multiparameter sonde (600XLM or 6600 EDS) with calibration cup and probe guard
2.2. YSI 650 display unit (sonde can be interfaced with computer; CRASR typically uses display unit for calibration and instantaneous sampling)
2.3. Cables to connect unit and sonde—there are field cables and one which is not watertight for non-field use only
2.4. CRASR YSI calibration and maintenance logbook
2.5. Ring stand
2.6. Glassware—Class A volumetric flasks and other standard glassware as needed
2.7. Deionized water
2.8. Balance—analytical, capable of accurately weighing to the nearest 0.0001 g
2.9. Calibration standards
2.9.1. Commercially purchased 4, 7, 10 pH buffer solutions

2.9.2. KCl for preparation of conductivity standard
2.9.3. Hach 4000 NTU formazin solution

2.10 CRASR multiprobe maintenance kit—a toolbox containing supplies needed for maintenance, including D.O. membranes, D.O. probe solution, special sandpaper supplied by YSI, conductivity block cleaning brush, O-ring lubricant, and any spare probes.

3. Calibration standards

3.1. pH buffer— 4,7, 10,commercially purchased; check expiration date before use

3.2. Conductivity— Dissolve 745.6 mg anhydrous KCl in deionized water and dilute to 1000 ml in a class A volumetric flask. May be stored in glass or plastic, at room temperature. This is the standard reference solution which at 25° C has a conductivity of 1412 umhos/ cm (Standard Methods 2510B).

3.3. Turbidity—Hach 4000 NTU formazin solution

4. Routine Maintenance

4.1 Routine maintenance is performed according to schedule outlined in the YSI manual and TCEQ SWQM procedures manual, or sooner if instrument performance is unacceptable.

4.2 All maintenance events are recorded in CRASR YSI calibration and maintenance logbook.

4.3 Routine maintenance tasks include: battery replacement, dissolved oxygen membrane replacement, polishing of dissolved oxygen electrode, cleaning of conductivity cell, greasing o-rings.

4.4 Maintenance supplies are kept in the CRASR multiprobe maintenance kit.

4.5 Refer to the YSI manual for step-by-step instructions for specific maintenance tasks and for troubleshooting performance problems.

5. Calibration Procedures

5.1. Instruments are calibrated within 24-hours prior to data collection

5.2. All calibrations are recorded in the CRASR YSI calibration and maintenance logbook. The data sheet for use in the logbook is included as Appendix A.

5.3. Instruments should be calibrated at room temperature, with all reagents, including deionized water, acclimated to room temperature.

5.4. **YSI 600 XLM (small data sondes)**— It is easiest and the smallest volume of standards are used if this sonde is calibrated with the calibration cup attached and sonde inverted (probes up). A ring stand may be useful when calibrating in this manner. Calibration with probes facing down is acceptable as long as probes are immersed (or not immersed) as specified in calibration procedures.

5.4.1. Conductivity

5.4.1.1.Connect sonde to the 650 MDS display unit, turn on, and access sonde menu

5.4.1.2.Rinse the probes several times with D.I. water followed by rinses with a small amount of standard solution. Shake vigorously when rinsing. Used standard may be maintained for this purpose.

5.4.1.3.Pour 1412 µmhos/cm conductivity standard into calibration cup so that it covers conductivity cell and temperature probe.

5.4.1.4.Allow at least one minute for temperature equilibration

5.4.1.5.From the Calibrate Menu, select 1-SpCond to access the specific conductance calibration procedure. Enter the calibration value of the standard and press Enter.

5.4.1.6.Observe Specific Conductance or Conductivity readings, when they show no significant change for approximately 30 seconds, press Enter. The screen will indicate that the calibration has been accepted; press Enter again and return to the Calibrate menu.

5.4.2. pH-- The pH buffers contain high concentrations of phosphate. During calibration, avoid leaving traces of buffer on equipment or at the work place that could contaminate water samples.

5.4.2.1.Rinse probes several times with D.I. water followed by pH 7 buffer, shaking vigorously while rinsing. Used buffer may be maintained for this purpose.

5.4.2.2.Place enough pH 7 buffer into the calibration cup to immerse the pH probe, reference junction, and temperature probe.

5.4.2.3.Allow at least one minute for the temperature to equilibrate.

5.4.2.4.From the Calibrate Menu, select 4-ISE 1 pH to access the pH calibration choices; then press 2-2 Point.

5.4.2.5.Press Enter and input the value of the buffer at the prompt.

5.4.2.6.Press Enter, and the current values of all enabled sensors will appear on the screen. Observe the pH mV reading. This value should range from -40 to +40.

5.4.2.7.Observe the pH reading and when it shows no significant change for approximately 30 seconds, press Enter. The display will indicate that the calibration is accepted.

5.4.2.8.After the pH 7 calibration is complete, press Enter again to continue. Rinse probes several times with D.I. water followed by pH 4 or 10 buffer, shaking vigorously while rinsing.

5.4.2.9.Calibrate instrument following same procedures as above.

6.4.2.10. pH mV reading should range from 140 to 220 in pH 4 buffer, or from –140 to –220 in pH 10 buffer.

6.4.3 Dissolved oxygen—instantaneous sampling

6.4.3.1 Disable the auto sleep function. From the Main Menu, select 8-Advanced and then 2-Setup. If the auto sleep functions are enabled, select 5-Auto Sleep RS232 and 6-Auto Sleep SDI12 and press Enter to disable.

6.4.3.2 Place about 1/8 inch of water in the bottom of the calibration cup. Make certain that the DO and temperature probes are not immersed in the water.

6.4.3.3 Gently place a paper towel at one edge of DO membrane so that water is wicked off the membrane.

6.4.3.4 Engage only one thread of the calibration cup to ensure the DO probe is vented to the atmosphere.

6.4.3.5 Wait at least 10 minutes for the air in the calibration cup to become water saturated and for the temperature to equilibrate.

6.4.3.6 From the Calibrate Menu, select 2-Dissolved Oxygen, then 1-DO% to access the DO% calibration procedure.

6.4.3.7 Enter the current barometric pressure in mm of Hg, obtained from the internal barometer of the 650 MDS display unit.

6.4.3.8 Observe the temperature and DO readings, and when there is no significant change for approximately 30 seconds, press Enter. The screen will indicate that the calibration has been accepted.

6.4.4 Dissolved oxygen—unattended monitoring

6.4.4.1 Enable autosleep function. From the Main Menu, select 8-Advanced and then 2-Setup. If the autosleep functions are not enabled, select 5-Auto Sleep RS232 and 6-Auto Sleep SDI12 and press Enter to enable.

6.4.4.2 Follow the calibration procedure described above.

6.4.4.3 Activate the countdown timer for the DO warm-up time. After DO warm-up is complete, the readings just before and after calibration are displayed. A message saying Press Enter to continue will appear. Press Enter and the screen will return to the DO calibration menu.

NOTE: the warm-up time should be set at 90 seconds

6.4.5 Depth and Temperature Sensor

6.4.5.1 Zero the depth sensor immediately before making the initial measurement with the instrument at the first station of the day.

6.4.5.2 Several times a year, or when a malfunction is suspected, check the temperature reading against an NBS thermometer to ensure suitable instrument performance. Record in logbook.

6.5 **YSI 6600 EDS (large data sondes)**—Due to the large volume of the calibration cup and of standards used, it is desirable to calibrate this unit with the probes facing down. A wall-mounted hook to hold the sonde due to its weight may be useful when calibrating in this manner. It may be useful to use a separate, smaller volume calibration cup that can fit around specific probes when possible. If this is done, ensure that temperature probe is also immersed for temperature compensated parameters (pH, conductivity). For dissolved oxygen, it may be easiest to calibrate with probes up, but either is acceptable as long as probes are not in water.

6.5.1 Conductivity, pH, dissolved oxygen, depth and temperature
6.5.1.1 Calibrate as outlined for the 650 XLM.
6.5.2 Turbidity
6.5.2.1 Rinse probes and calibration cup thoroughly with D.I. water. Shake to dry.
6.5.2.2 With the probes facing down (sonde hanging from hook or otherwise supported), use a graduated cylinder to measure 400 mls of D.I. water into the calibration cup

Note: the plastic cup with CRASR's sonde is black-bottomed and acceptable for use in calibration

6.5.2.3 Attach the cup loosely by engaging a few threads; probes will be immersed
6.5.2.4 Select 2-point turbidity from the calibration menu and input the 0 NTU value; press enter
6.5.2.5 Activate the wiper 1-2 times by pressing 3-clean optics
6.5.2.6 After readings have stabilized, press enter to confirm
6.5.2.7 Use a small graduated cylinder or pipette to add 2 ml of Hach 4000 NTU formazin standard to the calibration cup. Swirl to mix.
6.5.2.8 Repeat procedure above; second standard value is 20 NTU

6.5.3 Chlorophyll-a
6.5.3.1 Thoroughly rinse probes and calibration cup
6.5.3.2 Place an adequate amount of D.I. water into the calibration cup so that probes are immersed, and engage threads
6.5.3.3 Select Optic C -Chlorophyll from the Calibrate Menu, Chl µg/L and then 1-1 point.
6.5.3.4 Input the value 0 µg/L at the prompt, and press enter.
6.5.3.5 The screen will display real-time readings that will allow you to determine when the readings have stabilized. Activate the wiper 1-2 times by pressing 3-Clean Optics.
6.5.3.6 After stabilization is complete, press Enter to "confirm" the calibration and then, as instructed, press Enter to return to the Calibrate menu.

NOTE: This procedure will zero the fluorescence sensor and use the default sensitivity for calculation of chlorophyll concentration in µg/L. It may be desirable to periodically utilize additional procedures outlined in the YSI user's manual that describe the use of dyes or solutions with known chlorophyll concentrations to improve accuracy, depending on goals of study. Additionally, CRASR maintains records of Chl-a measurements obtained using the YSI compared to laboratory measurements for the same samples, which may be useful in assessing utility of the probe measurements.

7. **Collecting field data**

7.1 Refer to TCEQ SWQM manual for site selection considerations and depth of sampling.
7.2 Refer to YSI user's manual for specific questions regarding operation.

7.3 In general, instantaneous data will be collected at representative water body locations utilizing 650 MDS display unit.

7.4 Data may be recorded by hand on data sheets or logged into display unit.
7.5 Alternatively, sonde may be programmed for unattended monitoring prior to deployment.
7.6 Following data collection and post-calibration checks, any logged data will be downloaded onto laboratory computer utilizing EcoWatch for Windows software. Invalid or inapplicable data will be deleted.

8. Post-calibration checks

8.1 As soon as possible following data collection, record readings of standards of known value (as covered in calibration section) in the CRASR YSI calibration and maintenance logbook.
8.2 Do not actually calibrate the instrument.
8.3 Data collected when post-calibration checks are outside of these limits is of questionable quality and will be flagged.

Post-Calibration Check Error Limits

Parameter	Value
Dissolved oxygen	± 0.5 mg/L, ± 6% saturation
pH	± 0.5 standard units
Specific conductance	± 5%
Temperature ± 1 °C, annual calibration check	± 1 °C, annual calibration check
Depth ± 0.2 at 1 m, annual calibration check	± 0.2 at 1 m, annual calibration check

9. Quality Control/ Quality Assurance

9.1 CRASR YSI calibration and maintenance logbook is a primary record of quality control and quality assurance.
9.2 In addition to requirements listed throughout this SOP, the YSI 650 internal barometer is checked against an external barometer or uncorrected local value at least once a year. A record of this event is entered into the logbook.
9.3 See CRASR SOP #8 (Quality Assurance and Quality Control) for details on QA/ QC criteria.

Appendix B

CENTER FOR RESERVOIR AND AQUATIC SYSTEMS RESEARCH (CRASR)

STANDARD OPERATING PROCEDURE # Determination of TOC & DOC in water

Method Description

1.1. This method details the determination of Dissolved Organic Carbon and Total Organic Carbon in fresh waters by oxidative combustion and infrared analysis. This practical range of determination for this method as reported by the manufacturer is 0 – 25000 ug/L. This lab primarily uses NPOC to determine TOC and DOC in water and completes a separate run for inorganic C. The same procedure is used to determine both OC and IC, the only difference is the method which is inserted into the Auto Generate Wizard. Sample preservation is done by freezing rather than acidification.

Equipment and Supplies

2.1. Shimadzu TOC-V_{CSH} analyzer
Shimadzu ASI-V autosampler
High purity O_2 tank
Computer with TOC software installed

2.5. 20 ml borosilicate vials and septum caps

Sample Collection and Preservation

3.1. Samples collected in 50 ml plastic centrifuge tube
  3.1.1. Both filtered and non-filtered samples are collected for analysis
  3.1.2. Filtered samples are filtered using a 50-60 ml syringe and a 0.45 um polypropylene membrane filter

3.2. Sample vials are clearly labeled with Project and Site code, and date

3.3. Samples stored in cooler on ice and transported back to lab

3.4. Samples are frozen in laboratory freezer until processing

Preparation of Reagents

4.1. Preparation of Reagents
  4.1.1. *2N HCl*

Dilute one part concentrated hydrochloric acid with five parts DI water. A final concentration accuracy of ± 2% is acceptable.

4.2. Preparation of Standards

4.2.1. *Calibration Standards:*

Separate calibration standards are prepared for IC and OC.

For OC, we use a purchased standard of 1 mg C/mL and dilute a working standard to a concentration of 10 mg/L and then dilute two more calibration check standards at a concentration of 1 mg/L and 5 mg/L.

For IC, we prepare a stock standard of 1000 mg/L using 0.7 g $NaHCO_3$ + 0.88 g $NaCO_3$ in 200 ml/DI. From the stock standard, a 25 mg/L calibration check standard is created.

Procedure

5.1. Turn on **O_2**

5.2. Turn on **TOC-V_{CSH}**

5.3. Turn on Computer

5.4. Open TOC program

5.4.1. select **Sample Table Editor**

5.4.2. select new document or **Sample Run**

5.4.3. connect instrument to computer (**yellow lightning bolt**), select **Use Settings on PC**, stop light button should appear once connected

5.4.4. from the toolbar menu select **Insert** and **Auto Generate**

5.4.5. using the set-up wizard select the **Calibration Curve** or **Method** you are getting ready to run, then select **Next**

5.4.6. Enter the number of vials you are going to be running, then select **Next**

5.4.7. Select **OK** for **Sparging/Acid Addition**, select , then select **Finish**

5.5. Fill sample vials with Standard and Samples, then replace ASI cover on Autosampler

5.6. Check all water and Acid bottles to make sure they are at the appropriate level

5.7. Check pressure on TOC-V_{CSH} gages should read 200 and 150

5.8. Select the **Stop Light button** to start the run

5.9. When run is complete select the **Lightning Bolt** button to disconnect

5.10. Select the **Shutdown** option at left and select **Lightning Bolt** button to connect

5.11. Let the system run thru the shutdown and then turn off the **O_2** and the **TOC-V_{CSH}**

5.12. Procedure is the same for **TOC/DOC, NPOC** and **IC**

*Machine is not recalibrated for each run. The calibration curve is stored in the method and Check Standards are run at the beginning and end of each run to verify the calibration curve.

Quality Control/Quality Assurance – See CRASR SOP # 8 (Quality Assurance and Quality Control) for details on QA/QC Criteria.

References

7.1. Standard Methods For The Examination of Water and Wastewater, Method 5310 B; Total Organic Carbon (TOC), High-Temperature Combustion Method. American Public Health Association. 21st Edition, 2005.

7.2. Code of Federal Regulations. Protection of Environment. Section 40, Appendix B to Part 136. Definition and procedure for the determination of the method detection limit. Revision 1.11. Revised July 1, 1990. Office of the Federal Register, National Archives and Records.

7.3. ASTM. American Society for Testing and Materials. Standard Specifications for Reagent Water. D1193-77 (Reapproved 1983). Annual Book of ASTM Standards, Vol. 11.01. ASTM: Philadelphia, PA, 1991. DOC/TOC/CCAL 20A.0 June 2006 Page 10 of 10

7.4. Shimadzu TOC-V CPH/CPN & TOC-Control V Software User's Manual. Shimadzu Corporation; Analytical & Measuring Instruments Division; Kyoto, Japan.

7.5. EPA Method 415.1, Editorial Revision 1974. "Organic Carbon, Total (Combustion or Oxidation)", US Environmental Protection Agency; Washington DC.

7.6. US EPA, November 2004, Revision 1. "Total Organic Carbon", Method 9060A, SW-846, US Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.

This page intentionally left blank.

Appendix C

CENTER FOR RESERVOIR AND AQUATIC SYSTEMS RESEARCH (CRASR) STANDARD OPERATING PROCEDURE #7.0 – Determination of Total N in Water Analytical Range: 1 to 1000 µg N/L Revision 1 Adopted February 27, 2007

1. Method Description

Nitrate is measured in digested samples for determination of TN. Nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl)ethylenediamine dihydrochloride. The resulting water soluble dye has a magenta color which is read at 520 nm. Nitrite alone also can be determined by removing the cadmium column.

2. Equipment and Supplies

2.1. Balance -- analytical, capable of accurately weighing to the nearest 0.0001 g.

2.2. Glassware -- Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

2.3. Flow injection analysis equipment designed to deliver and react sample and reagents in the required order and ratios.

- 2.3.1. Autosampler
- 2.3.2. Multichannel proportioning pump
- 2.3.3. Reaction unit or manifold
- 2.3.4. Colorimetric detector
- 2.3.5. Data system
- 2.3.6. Acid washed glassware: All glassware used in the determination of phosphate should be washed with 10% muriatic acid and triple rinsed with distilled water. Preferable, this glassware should be used only for the determination of phosphate and after use it should be rinsed with distilled water and kept covered until needed again.

2.4. Special Apparatus:

- 2.4.1. Autoclave or Hot Plate

3. Sample Collection and Preservation – See CRASR SOP # 2 for details.

4. Standards

a. Nitrate-N Stock solution (1000 mg P/L) – Add 500 ml deionized water to a 1000 ml volumetric flask. Carefully weigh out 6.0677 g of ACS grade sodium nitrate (NaNO3; FW=84.99) and add it to the flask. Dissolve material, dilute to 1000 ml, and mix well. Solution may be stored indefinitely in refrigerator if also using a laboratory control standard (LCS) as a calibration verification in analyses. If not using LCS calibration verification, the Nitrate-N stock solution should be prepared fresh monthly.

b. DNP Mixed standard (10 mg P / L) – The DNP mixed standard is used for the simultaneous determination of PO4-P and NO2-N+NO3-N in unpreserved water samples. To prepare, add 250 ml of water to a 500 ml volumetric flask. Carefully pipette 5 ml of Nitrate-N Stock Solution and 5 ml of Phosphate-P Stock Solution into the flask. Dilute to 500 ml and mix well. The DNP Mixed standard may be stored in the refrigerator for up to 48 hours.

c. Mixed working standards – Mixed working standards are used as calibration and continuing calibration verification (CCVs) standards in the simultaneous determination of PO4-P and NO2-N+NO3-N. Prepare mixed working standards at concentrations of 5, 10, 25, 50, 100, 250, 500, and 1000 ppb (µg/L) PO4-P. The following table outlines preparation:

Mixed Working Standard (µg/L)	Volumetric Flask Size (ml)	DNP Mixed Standard concentration (µg/L)	Volume of Mixed Standard to Add to Volumetric (ml)
5	250	10,000	0.125
10	250	10,000	0.25
25	250	10,000	0.625
50	250	10,000	1.25
100	250	10,000	2.5
250	250	10,000	6.25
500	250	10,000	12.5
1000	250	10,000	25

Mixed working standards may be stored in the refrigerator for up to 48 hours.

d. Laboratory Control Standard – A laboratory control standard of 250 ppb should be prepared from a purchased certified aqueous nitrate-nitrogen standard. This standard should be certified by the external source from which it was purchased.

5. Reagents

Digestion Solution – Dissolve 20.1 g ACS grade (low nitrogen) potassium persulfate (K2S2O8) and 3.0 g NaOH in 1000ml DI water.

Borate Buffer Solution – Dissolve 61.8 g boric acid (H3BO3) and 8.0 g NaOH in 1000 ml DI water.

Degassing with helium:

To prevent bubble formation, degas all solutions except the standards with helium. Use He at 140kPa (20 lb/in^2) through a helium degassing tube (Lachat Part No. 50100.) Bubble He through the solution for one minute.

15 N Sodium Hydroxide

By Volume: Add **150 g NaOH** very slowly to **250 mL or g of water**. **CAUTION:** The solution will get very hot! Swirl until dissolved. Cool and store in a plastic bottle.

Ammonium Chloride buffer, pH 8.5

By Volume: In a **1 L** volumetric flask, dissolve **85.0 g ammonium chloride** (NH_4Cl) and **1.0 g disodium ethylenediamine tetraacetic acid dihydrate** ($Na_2EDTA{\cdot}2H_2O$) in about **800 mL water**. Dilute to the mark and invert to mix. Adjust the **pH to 8.5 with 15 N sodium hydroxide solution.**

ACS grade ammonium chloride has been found occasionally to contain significant nitrate contamination. An alternative recipe for the ammonium chloride buffer is:

By Volume: CAUTION: Fumes!!! In a hood, to a **1 L** volumetric flask, add **500 mL water**, **105 mL concentrated hydrochloric acid** (HCl), **95 mL ammonium hydroxide** (NH_4OH), and **1.0 g disodium EDTA**. Dissolve and dilute to the mark. Invert to mix. Adjust the **pH to 8.5 with HCl or 15 N NaOH solution.**

Sulfanilamide color reagent

By Volume: To a **1 L** volumetric flask, add about **600 mL water**. Then add **100 mL of 85% phosphoric acid** (H_3PO_4), **40.0 g sulfanilamide**, and **1.0 g N-(1-naphthyl)ethylenediamine dihydrochloride** (NED). Shake to wet, and stir for 30 min. to dissolve. Dilute to the mark, and invert to mix. Store in a dark bottle. This solution is stable for one month.

Carrier.

Combine 150 ml Digestion solution with 300 ml DI water. Autoclave with samples. After autoclaving, add 30 ml Borate Buffer Solution.

6. Procedure

6.1. Prepare reagent and standards as described in sections 4 and 5 of this document.

6.2. Add 10 ml of sample (or standard; all standards and blanks should be digested along with samples) to a digestion tube (borosilicate glass scintillation vial with open-top cap).

6.3. Add 5 ml digestion solution to each vial, cap tightly, and mix. Autoclave samples for 60 minutes using program 3 on the large autoclave on BSB 3rd floor. Program for autoclave should not include any drying time. After cycle has finished, remove samples from autoclave and allow them to cool to room temperature.

6.4. After samples have cooled to room temperature, add 1.0 ml Borate Buffer solution to each vial.

6.5. Set up nitrate manifold as shown in section 9 of this document (manifold diagram is on the last page of the SOP).

6.6. Make sure power is on to all portions of the instrument (autosampler, manifold pump, and main instrument) then open the Omnion software. On the main screen click on the "Configuration" pull down menu then click on "Autosamplers". When the pop up menu opens, click the button that says "Initialize Autosampler". This should cause the autosampler to re-center itself over the rinse tube then move permanently down into the rinse tube.

6.7. After you have initialized the autosampler, open the NO2-N+NO3-N and PO4-P template by going to the "Run" pull down menu and clicking on "Open". Navigate to the folder Omnion/templates and click on the file named NO2-N plus NO3-N and PO4-P.omn. When the file opens, the software will ask if you would like to change the setpoints of the relevant heaters. Click yes. Click again on the "Run" pull down menu, then click "Save As". Navigate to the folder Omnion/Data/Inorganic Nutrients. Save the template as the batch ID (yyyymmddPRJmANL; code on Chain of Custody Form) number associated with the sample set you are running. After the template has been saved, click the "Preview" button on the toolbar. This will allow you to view the baseline signal from the flowcell.

6.8. Secure the pump tubes to the pump by clicking down the tubing shafts. Turn on the pump by pressing the manual flow button on the top left of the pump (blue button). Make sure that the probe rinse pump line is submerged in DI water and that the probe is down in the rinse tube on the autosampler. Put all reagent lines into DI water. Pump DI water through all reagent lines and check for leaks and smooth flow. After any air in the system has passed through the flow cell, the baseline in the preview screen should be completely flat. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved. This will probably take at least 15 minutes for all chemicals to come into equilibrium in the mixture.

6.9. Place standards in the sampler according to the slot locations in the method template. Fill in samples with the appropriate duplicates and spikes. All information on duplicate and spike samples has already been set up in the template for the analytical method, the only thing that needs to change are the sample IDs.

6.10. Once all sample data has been entered into the sample sheet, save the run again as described earlier. Once saved, check the baseline to insure that

reagents have come through and that the baseline is stable. If stable, press the "Run" button on the tool bar.

6.11. The software will check that the LCS, and that all CCVs, duplicates, and spikes meet appropriate QA/QC criteria. If the LCS fails to meet QA/QC criteria, the run will automatically terminate. However, if the LCS passes and one of the CCVs, duplicates, or spikes fails to meet QA/QC criteria, the run will continue. It is imperative that the analyst check the QA/QC results for all CCVs, duplicates, and spikes and rerun any and all sample sets that do not adhere to QA/QC requirements outlined in CRASR SOP #8.

7. Quality Control/Quality Assurance – See CRASR SOP # 8 (Quality Assurance and Quality Control) for details on QA/QC criteria.

8. References

Lachat Procedures #10-107-04-1-C. Determination of nitrate/nitrite in surface and wastewaters by flow injection analysis.
U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and
Wastes, Method 353.2.
Methods for Determination of Inorganic Substances in Water and Fluvial Sediments. Book 5. Chapter A1. U.S. Department of the Interior, U.S. Geological Survey.

9. Instrument Information

DATA SYSTEM PARAMETERS FOR QUIKCHEM 8000

The timing values listed below are approximate and will need to be optimized using graphical events programming.

Sample throughput: 55 samples/h, 65 s/sample
Pump Speed: 35
Cycle Period: 65

Analyte Data:

Concentration Units: mg N/L
Peak Base Width: 25 s
% Width Tolerance: 100
Threshold: 5000
Inject to Peak Start: 22 s
Chemistry: Direct

Calibration Data:

Level	1	2	3	4	5	6	7
Concentration mg N/L	2.00	0.80	0.20	0.05	0.02	0.01	0.00

Calibration Rep Handling: Average
Calibration Fit Type: 1st Order Polynomial
Weighting Method: None
Force through zero: No

Sampler Timing:

Min. Probe in Wash Period: 12 s
Probe in Sample Period: 32 s

Valve Timing:

Load Time: 0 s
Load Period: 28 s
Inject Period: 37 s

Appendix D

CENTER FOR RESERVOIR AND AQUATIC SYSTEMS RESEARCH (CRASR) STANDARD OPERATING PROCEDURE #6.0 – Determination of Total P in Water Analytical Range: 1 to 1000 µg P/L Revision 1 Adopted February 27, 2007

1. Method Description

The orthophosphate ion (PO43-) reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex. This complex is reduced with ascorbic acid to form a blue complex, which absorbs light at 880 nm. The absorbance is proportional to the concentration of orthophosphate in the sample. Polyphosphates may be converted to the orthophosphate form by sulfuric acid digestion and organic phosphorus may be converted to orthophosphate by persulfate digestion.

2. Equipment and Supplies

2.1. Balance -- analytical, capable of accurately weighing to the nearest 0.0001 g.

2.2. Glassware -- Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

2.3. Flow injection analysis equipment designed to deliver and react sample and reagents in the required order and ratios.

2.3.1. Sampler

2.3.2. Multichannel proportioning pump

2.3.3. Reaction unit or manifold

2.3.4. Colorimetric detector

2.3.5. Data system

2.3.6. Acid washed glassware: All glassware used in the determination of phosphate should be washed in 10% muriatic acid and triple rinsed with distilled water. Preferably, this glassware should only be used in the determination of phosphate and after use it should be rinsed with distilled water and kept covered until needed again.

2.4. Special Apparatus:

2.4.1. Heating Unit Lachat Part No. A85X00 (X=1 for 110V, X=2 for 220V)

2.4.2. Autoclave or Hot Plate

3. Sample Collection and Preservation – See CRASR SOP #2 for details.

4. Standards

4.1. Phosphate-P Stock solution (1000 mg P/L) – Add 500 ml deionized water to a 1000 ml volumetric flask. Carefully weigh out 11.5641 g of sodium phosphate dibasic 12-hydrate ($Na_2HPO_4*12H_2O$; FW=358.14) and add it to the flask. Dissolve material, dilute to 1000 ml, and mix well. Solution may be stored indefinitely in refrigerator if also using a laboratory control standard (LCS) as a calibration verification in analyses. If not using LCS, stock solution should be prepared fresh monthly.
4.2. Phosphate Standard (10 mg P / L) – The phosphate standard is used for the determination of PO4-P in preserved and digested water samples. To prepare, add 250 ml of water to a 500 ml volumetric flask. Carefully pipette 5 ml of Phosphate-P Stock Solution into the flask. Dilute to 500 ml and mix well. Add 0.5 ml concentrated H_2SO_4. The phosphate standard may be stored in the refrigerator for up to 28 days.
4.3. Working standards – Working standards are used as calibration and continuing calibration verification (CCVs) standards in the determination of PO4-P in digested samples. Prepare working standards at concentrations of 5, 10, 25, 50, 100, 250, 500, and 1000 ppb (µg/L) PO4-P. The following table outlines preparation:

Working Standard (µg/L)	Volumetric Flask Size (ml)	Phosphate Standard concentration (µg/L)	Volume of Phosphate standard to Add to Volumetric (ml)
5	250	10,000	0.125
10	250	10,000	0.25
25	250	10,000	0.625
50	250	10,000	1.25
100	250	10,000	2.5
250	250	10,000	6.25
500	250	10,000	12.5
1000	250	10,000	25

Add concentrated H_2SO_4 to each standard to a final concentration of 0.1%. Standards may be stored in the refrigerator for up to 28 days.
4.4. Laboratory Control Standard – A laboratory control standard of 250 ppb should be prepared from a purchased certified aqueous phosphate-phosphorus standard. This standard should be certified by the external source from which it was purchased.

5. Reagents

Degassing with helium:

To prevent bubble formation, degas all solutions except the standards with helium. Use He at 140kPa (20 lb/in^2) through a helium degassing tube (Lachat Part No. 50100.) Bubble He through the solution for one minute.

Reagent 1. Stock Ammonium Molybdate Solution

By Weight: To a tared **1 L** container add **40.0 g ammonium molybdate tetrahydrate** [$(NH_4)_6Mo_7O_{24}.4H_2O$] and **983 g DI water**. Stir for a minimum of four hours. Store in plastic and refrigerate.

Reagent 2. Stock Antimony Potassium Tartrate Solution

By Weight: To a **1 L** dark, tared container add **3.0 g antimony potassium tartrate** (potassium antimonyl tartrate hemihydrate $K(SbO)C_4H_4O_6.1/2H_2O$) or dissolve **3.22 g antimony potassium tartrate** (potassium antimonyl tartrate trihydrate $C_8H_4O_{12}K_2Sb_2$ $3H_2O$) and **995 g DI water.** Stir or shake until dissolved. Refrigerate. Maybe stored up to two months when kept refrigerated.

Reagent 3. Molybdate Color Reagent

By Volume: To a **1 L** volumetric flask add about **500 mL DI water**, and then add **21.0 mL concentrated sulfuric acid** (CAUTION: The solution will get very hot!). Swirl to mix. When it can be comfortably handled, add **72.0 mL Stock Antimony Potassium Tartrate Solution** (Reagent 2) and **213 mL Ammonium Molybdate Solution** (Reagent 1). Dilute to the mark **DI water** and invert to mix.

Reagent 4. Ascorbic Acid Reducing Solution, 0.33 M

By Weight: To a tared **1 L** container, add **60.0 g granular ascorbic acid and 975 g DI water**. Stir or shake until dissolved. Add **1.0 g dodecyl sulfate** ($CH_3(CH_2)_{11}OSO_3Na$). Prepare fresh weekly. Discard if the solution becomes yellow.

Reagent 5. Carrier: Sulfuric Acid with Persulfate

By Volume: In a **1 L** volumetric flask, add **500 mL DI water**, **10 g potassium persulfate**, and **2.0 mL concentrated sulfuric acid** (H_2SO_4). Dilute to the mark **DI water** and invert to mix. Degas daily. Prepare fresh weekly.

6. Procedure

6.1. Prepare reagent and standards as described in sections 4 and 5 of this document.

6.2. Transfer 10 ml of each blank, standard, and sample to a digestion tube (borosilicate scinatillation vial with open-top cap). Add 0.0948 g of potassium persulfate (K2S2O8). Cap samples tightly and mix thoroughly. Autoclave samples for 60

minutes using program 3 on the large autoclave on BSB 3rd floor. Program for autoclave should not include any drying time. After cycle has finished, remove samples from autoclave and allow them to cool to room temperature.

6.2. Set up phosphorus manifold as shown in section 9 of this document (manifold diagram is on the last page of the SOP).

6.3. Make sure power is on to all portions of the instrument (autosampler, manifold pump, and main instrument) then open the Omnion software. On the main screen click on the "Configuration" pull down menu then click on "Autosamplers". When the pop up menu opens, click the button that says "Initialize Autosampler". This should cause the autosampler to re-center itself over the rinse tube then move permanently down into the rinse tube.

6.3. After you have initialized the autosampler, open the total P in waters template by going to the "Run" pull down menu and clicking on "Open". Navigate to the folder Omnion/templates and click on the file named total-P-water.omn. When the file opens, the software will ask if you would like to change the setpoints of the relevant heaters. Click yes. Click again on the "Run" pull down menu, then click "Save As". Navigate to the folder Omnion/Data/Inorganic Nutrients. Save the template as the batch ID (yyyymmddPRJmANL; code on Chain of Custody Form) number associated with the sample set you are running. After the template has been saved, click the "Preview" button on the toolbar. This will allow you to view the baseline signal from the flowcell.

6.3. Secure the pump tubes to the pump by clicking down the tubing shafts. Turn on the pump by pressing the manual flow button on the top left of the pump (blue button). Make sure that the probe rinse pump line is submerged in DI water and that the probe is down in the rinse tube on the autosampler. Put all reagent lines into DI water. Pump DI water through all reagent lines and check for leaks and smooth flow. After any air in the system has passed through the flow cell, the baseline in the preview screen should be completely flat. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved. This will probably take at least 15 minutes for all chemicals to come into equilibrium in the mixture.

6.4. Place standards in the sampler according to the slot locations in the method template. Fill in samples with the appropriate duplicates and spikes. All information on duplicate and spike samples has already been set up in the template for the analytical method, the only thing that needs to change are the sample IDs.

6.5. Once all sample data has been entered into the sample sheet, save the run again as described earlier. Once saved, check the baseline to insure that reagents have come through and that the baseline is stable. If stable, press the "Run" button on the tool bar.

6.6. The software will check that the LCS, and that all CCVs, duplicates, and spikes meet appropriate QA/QC criteria. If the LCS fails to meet QA/QC criteria, the run will automatically terminate. However, if the LCS passes and one of the CCVs, duplicates, or spikes fails to meet QA/QC criteria, the run will continue. It is

imperative that the analyst check the QA/QC results for all CCVs, duplicates, and spikes and rerun any and all sample sets that do not adhere to QA/QC requirements outlined in CRASR SOP #8.

7. Quality Control/Quality Assurance – See CRASR SOP # 8 (Quality Assurance and Quality Control) for details on QA/QC criteria.

8. References

Lachat Method # 10-115-01-1-F, Determination of total phosphorus by flow injection analysis colorimetry (acid persulfate digestion method).
U.S. Environmental Protection Agency, Methods for the Determination of Inorganic Substances in Environmental Samples, EPA-600/R-93/100, August 1993, Method 365.1
Methods for Determination of Inorganic Substances in Water and Fluvial Sediments. Book 5. Chapter A1. U.S. Department of the Interior, U.S. Geological Survey, Method I-2601-85.
Standard Methods for the Examination of Water and Wastewater, 18th Edition, p. 4 - 116, Method 4500-P F (1992)

9. Instrument Information

TABLE, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

DATA SYSTEM PARAMETERS FOR QUIKCHEM 8000

The timing values listed below are approximate and will need to be optimized using graphical events programming.

Sample throughput: 60 samples/h, 60 s/sample
Pump Speed: 35
Cycle Period: 60

Analyte Data:

Concentration Units: µg P/L
Chemistry Brackish
Inject to BW Baseline Start 10 s
Inject to BW Baseline End 65 s
Inject to BW Integ Start 25 s
Inject to BW Integ End 60 s

Calibration Data:

Level	1	2	3	4	5	6	7
Concentration µg P/L	200	100	50	25	10	3.0	0.0

Calibration Rep Handling: Average
Calibration Fit Type: 2nd Order Polynomial
Weighting Method: None
Force through zero: No

Sampler Timing:

Min. Probe in Wash Period: 10 s
Probe in Sample Period: 23 s

Valve Timing:

Load Time: 0 s
Load Period: 18 s
Inject Period: 42 s

Appendix E

CENTER FOR RESERVOIR AND AQUATIC SYSTEMS RESEARCH (CRASR) STANDARD OPERATING PROCEDURE #5.0 – Determination of NH3-N in Water Analytical Range: 10 to 1000 µg N/L Revision 1 Adopted February 27, 2007

1. Method Description

This method is based on the Berthelot reaction. Ammonia reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue. Sodium nitroprusside (nitroferricyanide) is added to enhance sensitivity. The absorbance of the reaction product is measured at 630 nm, and is directly proportional to the original ammonia concentration in the sample.

2. Equipment and Supplies

2.1. Balance -- analytical, capable of accurately weighing to the nearest 0.0001 g.

2.2. Glassware -- Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

2.3. Flow injection analysis equipment designed to deliver and react sample and reagents in the required order and ratios.

2.3.1. Autosampler

2.3.2. Multichannel proportioning pump

2.3.3. Reaction unit or manifold

2.3.4. Colorimetric detector

2.3.5. Data system

2.3.6. Acid washed glassware: All glassware used in the determination of phosphate should be washed with 10% muriatic acid and triple rinsed with distilled water. Preferable, this glassware should be used only for the determination of phosphate and after use it should be rinsed with distilled water and kept covered until needed again.

2.4. Special Apparatus

2.4.1. Heating unit Lachat Part No. A85X00 (X=1 for 110V, X=2 for 220V)

2.4.2. Glass calibration vials must be used. Lachat Part No. 21304 for XYZ samplers.

2.4.3. PVC PUMP TUBES MUST BE USED FOR THIS METHOD

3. Sample Collection and Preservation – See CRASR SOP # 2 for details.

4. Standards

a. Ammonia-N Stock solution (1000 mg N/L) – Add 500 ml deionized water to a 1000 ml volumetric flask. Carefully weigh out 3.8188 g of ammonium chloride (NH4Cl; FW=53.49) and add it to the flask. Dissolve material, dilute to 1000 ml, and mix well. Solution may be stored indefinitely in refrigerator if also using a laboratory control standard (LCS) as a calibration verification in analyses. If not using LCS as a calibration verification, the ammonia-N stock solution should be prepared fresh monthly.

b. DNP Mixed Standard (10 mg N / L) – The Mixed Standard is used for the determination of NH3-N in fresh water samples. To prepare, add 250 ml of water to a 500 ml volumetric flask. Carefully pipette 5 ml of Ammonia-N Stock Solution into the flask then dilute with DI water to 500 ml and mix well.

c. Mixed working standards – Mixed working standards are used as calibration and continuing calibration verification (CCVs) standards in the determination of NH3-N, which is run simultaneously with PO4-P and NO2-N+NO3-N. Prepare working standards at concentrations of 5, 10, 25, 50, 100, 250, 500, and 1000 ppb (µg/L) NH3-N. The following table outlines preparation:

Mixed Working Standard (µg/L)	Volumetric Flask Size (ml)	NH3-N Standard concentration (µg/L)	Volume of Mixed Standard to Add to Volumetric (ml)
5	250	10,000	0.125
10	250	10,000	0.25
25	250	10,000	0.625
50	250	10,000	1.25
100	250	10,000	2.5
250	250	10,000	6.25
500	250	10,000	12.5
1000	250	10,000	25

d. Laboratory Control Standard – A laboratory control standard of 250 ppb should be prepared from a purchased certified aqueous ammonia-nitrogen standard. This standard should be certified by the external source from which it was purchased.

5. Reagents

Degassing with helium:

To prevent bubble formation, degas all solutions except the standards with helium. Use He at 140kPa (20 lb/in^2) through a helium degassing tube (Lachat Part No. 50100.) Bubble He through the solution for one minute.

Reagent 1. Sodium Phenolate

CAUTION: Wear gloves. Phenol causes severe burns and is rapidly absorbed into the body through the skin.

By Volume: In a **1 L volumetric flask** dissolve **88 mL** of **88% liquefied phenol** or **83 g crystalline phenol** (C_6H_5OH) in approximately **600 mL DI water**. While stirring, slowly add **32 g sodium hydroxide** (NaOH). Cool, dilute to the mark, and invert to mix. Do not degas this reagent. Prepare fresh every 3 to 5 days. Discard when reagent turns dark brown.

Reagent 2. Sodium Hypochlorite

By Volume: In a **500 mL volumetric flask,** dilute **250 mL 5.25% sodium hypochlorite** (NaOCl), to the mark with **DI water**. Invert to mix. Prepare fresh daily

Reagent 3. Buffer

By Volume: In a **1 L volumetric flask**, dissolve **50.0 g disodium ethylenediamine tetraacetate dihydrate** ($Na_2EDTA \cdot 2H_20$) and **9.0 g sodium hydroxide** (NaOH) in approximately **900 mL DI water.** Dilute to the mark and mix with a magnetic stirrer until dissolved. Prepare fresh monthly

Reagent 4. Sodium Nitroprusside

By Volume: To a **1 L volumetric flask,** dissolve **3.50 g sodium nitroprusside** (Sodium Nitroferricyanide [$Na_2Fe(CN)_5NO.2H_2O$]). Dilute to the mark with **DI water** and invert to mix. Prepare fresh every 1 to 2 weeks

Reagent 5. Carrier and Diluent (DI water)

6. Procedure

6.1. Prepare reagent and standards as described in sections 4 and 5 of this document.

6.2. Set up ammonia manifold as shown in section 9 of this document (manifold diagram is on the last page of the SOP).

6.3. Make sure power is on to all portions of the instrument (autosampler, manifold pump, and main instrument) then open the Omnion software. On the main screen click on the "Configuration" pull down menu then click on "Autosamplers". When the pop up menu opens, click the button that says

"Initialize Autosampler". This should cause the autosampler to re-center itself over the rinse tube then move permanently down into the rinse tube.

6.3. After you have initialized the autosampler, open the NH3-N template by going to the "Run" pull down menu and clicking on "Open". Navigate to the folder Omnion/templates and click on the file named NH3-N.omn. When the file opens, the software will ask if you would like to change the setpoints of the relevant heaters. Click yes. Click again on the "Run" pull down menu, then click "Save As". Navigate to the folder Omnion/Data/Inorganic Nutrients. Save the template as the batch ID (yyyymmddPRJmANL; code on Chain of Custody Form) number associated with the sample set you are running. After the template has been saved, click the "Preview" button on the toolbar. This will allow you to view the baseline signal from the flowcell.

6.3. Secure the pump tubes to the pump by clicking down the tubing shafts. Turn on the pump by pressing the manual flow button on the top left of the pump (blue button). Make sure that the probe rinse pump line is submerged in DI water and that the probe is down in the rinse tube on the autosampler. Put all reagent lines into DI water. Pump DI water through all reagent lines and check for leaks and smooth flow. After any air in the system has passed through the flow cell, the baseline in the preview screen should be completely flat. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved. This will probably take at least 15 minutes for all chemicals to come into equilibrium in the mixture.

6.4. Place standards in the sampler according to the slot locations in the method template. Fill in samples with the appropriate duplicates and spikes. All information on duplicate and spike samples has already been set up in the template for the analytical method, the only thing that needs to change are the sample IDs.

6.5. Once all sample data has been entered into the sample sheet, save the run again as described earlier. Once saved, check the baseline to insure that reagents have come through and that the baseline is stable. If stable, press the "Run" button on the tool bar.

6.6. The software will check that the LCS, and that all CCVs, duplicates, and spikes meet appropriate QA/QC criteria. If the LCS fails to meet QA/QC criteria, the run will automatically terminate. However, if the LCS passes and one of the CCVs, duplicates, or spikes fails to meet QA/QC criteria, the run will continue. It is imperative that the analyst check the QA/QC results for all CCVs, duplicates, and spikes and rerun any and all sample sets that do not adhere to QA/QC requirements outlined in CRASR SOP #8.

6.7. After run is completed, place all reagent lines in 10% H2SO4 for at least 20 minutes. After this time, transfer all lines to DI water for an additional 30 minutes.

7. Quality Control/Quality Assurance – See CRASR SOP # 8 (Quality Assurance and Quality Control) for details on QA/QC criteria.

8. References

Lachat Method # 10-107-06-1-B. Determination of ammonia (phenolate) by flow injection analysis colorimetry.

U.S. Environmental Protection Agency, **Methods for Chemical Analysis of Water and Wastes**, EPA-600/4-79-020, Revised March 1983, Method 350.1

U.S. Environmental Protection Agency, 40 CFR, Part 36 Table 1B, footnote 6, 1994.

9. Instrument Information

DATA SYSTEM PARAMETERS FOR QUIKCHEM 8000

The timing values listed below are approximate and will need to be optimized using graphical events programming.

Sample throughput: 60 samples/h, 60 s/sample

Pump Speed: 35

Cycle Period: 60

Analyte Data:

Concentration Units: mg N/L

Peak Base Width: 29 s

% Width Tolerance: 100

Threshold: 10000

Inject to Peak Start: 30 s

Chemistry: Direct

Calibration Data:

Level	1	2	3	4	5	6	7
Concentration mg N/L	5.00	2.50	1.25	0.50	0.10	0.05	0.00

Calibration Rep Handling: Average

Calibration Fit Type: 1st Order Polynomial

Weighting Method: None

Force through zero: No

Sampler Timing:

Min. Probe in Wash Period: 5.0 s

Probe in Sample Period: 24 s

Valve Timing:

Load Time: 0 s

Load Period: 15 s

Inject Period: 45 s

Appendix F

CENTER FOR RESERVOIR AND AQUATIC SYSTEMS RESEARCH (CRASR) STANDARD OPERATING PROCEDURE #4.0 – Determination of NO2-N+NO3-N in Water Analytical Range: 1 to 1000 µg N/L Revision 0 Adopted April 1, 2006

1. Method Description

Nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl)ethylenediamine dihydrochloride. The resulting water soluble dye has a magenta color which is read at 520 nm. Nitrite alone also can be determined by removing the cadmium column.

2. Equipment and Supplies

2.1. Balance -- analytical, capable of accurately weighing to the nearest 0.0001 g.

2.2. Glassware -- Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

2.3. Flow injection analysis equipment designed to deliver and react sample and reagents in the required order and ratios.

2.3.1. Autosampler

2.3.2. Multichannel proportioning pump

2.3.3. Reaction unit or manifold

2.3.4. Colorimetric detector

2.3.5. Data system

2.3.6. Acid washed glassware: All glassware used in the determination of phosphate should be washed with 10% muriatic acid and triple rinsed with distilled water. Preferable, this glassware should be used only for the determination of phosphate and after use it should be rinsed with distilled water and kept covered until needed again.

3. Sample Collection and Preservation – See CRASR SOP # 2 for details.

4. Standards

a. Nitrate-N Stock solution (1000 mg P/L) – Add 500 ml deionized water to a 1000 ml volumetric flask. Carefully weigh out 6.0677 g of ACS grade sodium nitrate (NaNO3; FW=84.99) and add it to the flask. Dissolve material, dilute

to 1000 ml, and mix well. Solution may be stored indefinitely in refrigerator if also using a laboratory control standard (LCS) as a calibration verification in analyses. If not using LCS calibration verification, the Nitrate-N stock solution should be prepared fresh monthly.

b. DNP Mixed standard (10 mg P / L) – The DNP mixed standard is used for the simultaneous determination of PO4-P and NO2-N+NO3-N in unpreserved water samples. To prepare, add 250 ml of water to a 500 ml volumetric flask. Carefully pipette 5 ml of Nitrate-N Stock Solution and 5 ml of Phosphate-P Stock Solution into the flask. Dilute to 500 ml and mix well. The DNP Mixed standard may be stored in the refrigerator for up to 48 hours.

c. Mixed working standards – Mixed working standards are used as calibration and continuing calibration verification (CCVs) standards in the simultaneous determination of PO4-P and NO2-N+NO3-N. Prepare mixed working standards at concentrations of 5, 10, 25, 50, 100, 250, 500, and 1000 ppb (µg/L) PO4-P. The following table outlines preparation:

Mixed Working Standard (µg/L)	Volumetric Flask Size (ml)	DNP Mixed Standard concentration (µg/L)	Volume of Mixed Standard to Add to Volumetric (ml)
5	250	10,000	0.125
10	250	10,000	0.25
25	250	10,000	0.625
50	250	10,000	1.25
100	250	10,000	2.5
250	250	10,000	6.25
500	250	10,000	12.5
1000	250	10,000	25

Mixed working standards may be stored in the refrigerator for up to 48 hours.

d. Laboratory Control Standard – A laboratory control standard of 250 ppb should be prepared from a purchased certified aqueous nitrate-nitrogen standard. This standard should be certified by the external source from which it was purchased.

5. Reagents

Degassing with helium:

To prevent bubble formation, degas all solutions except the standards with helium. Use He at 140kPa (20 lb/in^2) through a helium degassing tube (Lachat Part No. 50100.) Bubble He through the solution for one minute.

Reagent 1. 15 N Sodium Hydroxide

By Volume: Add **150 g NaOH** very slowly to **250 mL or g of water**. **CAUTION:** The solution will get very hot! Swirl until dissolved. Cool and store in a plastic bottle.

Reagent 2. Ammonium Chloride buffer, pH 8.5

By Volume: In a **1 L** volumetric flask, dissolve **85.0 g ammonium chloride** (NH_4Cl) and **1.0 g disodium ethylenediamine tetraacetic acid dihydrate** ($Na_2EDTA \cdot 2H_2O$) in about **800 mL water**. Dilute to the mark and invert to mix. Adjust the **pH to 8.5 with 15 N sodium hydroxide solution.**

ACS grade ammonium chloride has been found occasionally to contain significant nitrate contamination. An alternative recipe for the ammonium chloride buffer is:

By Volume: CAUTION: Fumes!!! In a hood, to a **1 L** volumetric flask, add **500 mL water**, **105 mL concentrated hydrochloric acid** (HCl), **95 mL ammonium hydroxide** (NH_4OH), and **1.0 g disodium EDTA**. Dissolve and dilute to the mark. Invert to mix. Adjust the **pH to 8.5 with HCl or 15 N NaOH solution.**

Reagent 3. Sulfanilamide color reagent

By Volume: To a **1 L** volumetric flask, add about **600 mL water**. Then add **100 mL of 85% phosphoric acid** (H_3PO_4), **40.0 g sulfanilamide**, and **1.0 g N-(1-naphthyl)ethylenediamine dihydrochloride** (NED). Shake to wet, and stir for 30 min. to dissolve. Dilute to the mark, and invert to mix. Store in a dark bottle. This solution is stable for one month.

6. Procedure

6.1. Prepare reagent and standards as described in sections 4 and 5 of this document.

6.2. Set up nitrate manifold as shown in section 9 of this document (manifold diagram is on the last page of the SOP).

6.3. Make sure power is on to all portions of the instrument (autosampler, manifold pump, and main instrument) then open the Omnion software. On the main screen click on the "Configuration" pull down menu then click on "Autosamplers". When the pop up menu opens, click the button that says "Initialize Autosampler". This should cause the autosampler to re-center itself over the rinse tube then move permanently down into the rinse tube.

6.3. After you have initialized the autosampler, open the NO2-N+NO3-N and PO4-P template by going to the "Run" pull down menu and clicking on

"Open". Navigate to the folder Omnion/templates and click on the file named NO2-N plus NO3-N and PO4-P.omn. When the file opens, the software will ask if you would like to change the setpoints of the relevant heaters. Click yes. Click again on the "Run" pull down menu, then click "Save As". Navigate to the folder Omnion/Data/Inorganic Nutrients. Save the template as the batch ID (yyyymmddPRJmANL; code on Chain of Custody Form) number associated with the sample set you are running. After the template has been saved, click the "Preview" button on the toolbar. This will allow you to view the baseline signal from the flowcell.

6.3. Secure the pump tubes to the pump by clicking down the tubing shafts. Turn on the pump by pressing the manual flow button on the top left of the pump (blue button). Make sure that the probe rinse pump line is submerged in DI water and that the probe is down in the rinse tube on the autosampler. Put all reagent lines into DI water. Pump DI water through all reagent lines and check for leaks and smooth flow. After any air in the system has passed through the flow cell, the baseline in the preview screen should be completely flat. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved. This will probably take at least 15 minutes for all chemicals to come into equilibrium in the mixture.

6.4. Place standards in the sampler according to the slot locations in the method template. Fill in samples with the appropriate duplicates and spikes. All information on duplicate and spike samples has already been set up in the template for the analytical method, the only thing that needs to change are the sample IDs.

6.5. Once all sample data has been entered into the sample sheet, save the run again as described earlier. Once saved, check the baseline to insure that reagents have come through and that the baseline is stable. If stable, press the "Run" button on the tool bar.

6.6. The software will check that the LCS, and that all CCVs, duplicates, and spikes meet appropriate QA/QC criteria. If the LCS fails to meet QA/QC criteria, the run will automatically terminate. However, if the LCS passes and one of the CCVs, duplicates, or spikes fails to meet QA/QC criteria, the run will continue. It is imperative that the analyst check the QA/QC results for all CCVs, duplicates, and spikes and rerun any and all sample sets that do not adhere to QA/QC requirements outlined in CRASR SOP #8.

7. Quality Control/Quality Assurance – See CRASR SOP # 8 (Quality Assurance and Quality Control) for details on QA/QC criteria.

8. References

Lachat Procedures #10-107-04-1-C. Determination of nitrate/nitrite in surface and wastewaters by flow injection analysis.

U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, Method 353.2.

Methods for Determination of Inorganic Substances in Water and Fluvial Sediments. Book 5. Chapter A1. U.S. Department of the Interior, U.S. Geological Survey.

9. Instrument Information

DATA SYSTEM PARAMETERS FOR QUIKCHEM 8000

The timing values listed below are approximate and will need to be optimized using graphical events programming.

Sample throughput: 55 samples/h, 65 s/sample

Pump Speed: 35

Cycle Period: 65

Analyte Data:

Concentration Units: mg N/L

Peak Base Width: 25 s

% Width Tolerance: 100

Threshold: 5000

Inject to Peak Start: 22 s

Chemistry: Direct

Calibration Data:

Level	1	2	3	4	5	6	7
Concentration mg N/L	2.00	0.80	0.20	0.05	0.02	0.01	0.00

Calibration Rep Handling: Average

Calibration Fit Type: 1st Order Polynomial

Weighting Method: None

Force through zero: No

Sampler Timing:

Min. Probe in Wash Period: 12 s

Probe in Sample Period: 32 s

Valve Timing:

Load Time: 0 s

Load Period: 28 s

Inject Period: 37 s

This page intentionally left blank.

Appendix G

DIGESTION OF SEDIMENT OR SOIL FOR THE DETERMINATION OF TOTAL RECOVERABLE TRACE METALS

1.0 INTRODUCTION

This document provides the procedures which are used by staff of the Geochemical and Environmental Research Group (GERG) of the College of Geosciences at Texas A&M University for the digestion of soil, sludge, sediment and other geological samples prior to the determination of total recoverable trace metals.

1.1 Summary

This procedure describes the preparation of soil, sediment and similar geologic samples for all total recoverable trace metals except mercury, which requires a separate digestion process. The concentration of trace metals in sediment, soil and other geological materials can vary widely due to differences in particle size distribution, organic matter content, mineralogy of source materials, geochemical processes, and the impact of human activities.

Before samples can be analyzed, they must be converted from solid to liquid form using an acid digestion. Wet samples are homogenized in their container, and an aliquot is freeze dried and homogenized to a fine powder. Approximately 1.00 gram of powdered sediment is weighed into a beaker. Then HNO_3 and H_2O_2 (or other acids if necessary) are added and the mixture is heated at 95°C. After this acid digestion, the digestate is diluted to specific volume with reagent water, mixed and either filtered or allowed to settle overnight before analysis if required. The digestates are then analyzed for trace metals using appropriate instrumental SOP.

This method is **NOT** a total digestion technique. It is a very strong acid digestion that will dissolve many elements that could become "environmentally available." Elements bound in silicate structures are not normally dissolved by this procedure, and are not usually mobile in the environment. If total digestion is required, use the appropriate SOP.

1.2 Applicability

The digestate preparation procedures described in this document are applicable to sediment, sludge, soil and other geological sample matrices. Arsenic, cadmium, lead, selenium, silver, and thallium are typically determined using the GFAA technique, while other total extractable trace elements can be determined using the ICP technique.

1.3 Interferences

Method interferences can be caused by contaminants associated with reagents, reaction vessels, or sample preparation hardware, leading to increased trace metal concentrations in the digest solution. Interferences may result in a deviation from reported values in reference materials of a similar matrix type. All materials used in this method are routinely demonstrated to be free from added metals by processing procedural blanks in a manner identical to samples (1 blank per 20 samples or each batch, whichever is more frequent).

Compounds other than the trace elements (i.e., sulfur, organic material, carbonaceous material, etc.) in the sample matrix may also cause matrix interference.

Boron and silica from the glassware may be released into the solution during the acid digestion. For specific determinations of boron and silica, only quartz and/or PTFE plastic labware should be used. A series of laboratory blanks may be used to monitor and indicate a known contamination effect.

2.0 GENERAL SAFETY

The hazards, toxicity or carcinogenicity of each compound or reagent used in GERG standard operating procedures have not been precisely determined. However, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. The laboratory maintains Material Safety Data Sheets (MSDS) which contain information regarding the safe handling of chemicals used at GERG facilities. A reference file of MSDS is available to all personnel involved with these materials. All laboratory personnel should direct any questions regarding safety issues to their supervisors or the Safety Officer.

2.1 Specific Safety Procedures

The acidification of samples containing reactive materials may result in the release of toxic gases such as cyanides or sulfides. All acidification of samples should be done in a fume hood.

Concentrated hydrochloric acid and concentrated nitric acid are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a hood whenever possible. If eye or skin contact occurs, flush with large volume of water. Always wear safety glasses and acid resistant gloves when handling these reagents.

3.0 QUALITY CONTROL

A prime consideration in the determination of trace elements are possible contamination and digestate loss. Potential contamination sources include improperly cleaned labware and the dust from working area, etc. A clean laboratory area should be designated for the digestion of samples. It is always recommended that the bench and other working area be cleaned prior to digestion. All reusable labware should be sufficiently clean for the task objectives.

Several steps are involved in the cleaning of labware, which include:

- Soaking labware overnight and thoroughly washing with laboratory grade detergent and water.
- Rinsing labware with tap water, and rinsing with reagent water once to extend the life of the acid bath.
- Soaking labware for 8 hours or longer in an acid bath of 50% (V/V) nitric acid or a mixture of dilute nitric and hydrochloric acid as necessary.
- Rinsing labware with reagent water.
- Storing cleaned and dried labware in a dust-free environment.

The Quality Control (QC) samples described in the following sections are processed in a manner identical to actual samples.

3.1 Method Blanks

One method blank (also referred to as a procedural blank) is prepared with every 20 samples or with every QC batch, whichever is more frequent. The blank is prepared using all reagents and procedures for digestion, but does not contain any sample matrix. QC criteria for blank performance can be found in the appropriate analytical SOP.

3.2 Certified Reference Materials

If available, certified soil or sediment reference materials, as closely matching the sample matrix as possible, are prepared with each QC batch. The certified reference material is digested and analyzed to evaluate overall accuracy of the procedures used for sample preparation and analysis. Criteria for reference material performance can be found in the appropriate analytical SOP.

3.3 Duplicates

One duplicate, if sample material is sufficient, is prepared with every 20 samples or with every QC batch, whichever is more frequent. Duplicates provide a measure of sample homogeneity and of analytical precision. Criteria for duplicate performance can be found in the appropriate analytical SOP.

3.4 Matrix Spikes

One matrix spike, if sample material is sufficient, is prepared with every 20 samples or with every QC batch, whichever is more frequent. The matrix spike (MS) is a fortified sample that is carried through the digestion procedure, and analyzed to identify any matrix dependent interferences. The MS is used to evaluate the accuracy and performance of the analytical system. If requested a matrix spike duplicate (MSD) can be prepared, which provides information regarding homogeneity (precision) of the soil or sediment matrix. Criteria for matrix spike performance can be found in the appropriate analytical SOP.

3.5 Laboratory Blank Spikes (LBS)

One laboratory blank spike (LBS), a method blank fortified with appropriate trace elements and carried through the digestion procedure, can be prepared with every 20 samples or with every QC batch, whichever is more frequent. Lab blank spikes (LBS) are analyzed if there is inadequate sample available, if there is a difficult sample matrix, to identify any digestion interferences, and to evaluate the accuracy and performance of the analytical system. Criteria for LBS performance can be found in the appropriate analytical SOP.

4.0 APPARATUS AND MATERIALS

4.1 Labware and Apparatus

Mortar and Pestle: To grind and homogenize freeze-dried samples.

Glass Beakers: 200-mL Pyrex beakers or equivalent.

PTFE and/or Quartz Beakers (Optional): 200 ml with PTFE covers, for digestion of samples involved in the determination of boron and silica.

Watch Glass: 80-mm in diameter or big enough to cover the lip of beaker.

Hot Plate: Adjustable temperature, capable of maintaining a temperature of 95°C.

Microliter pipettes: 1000-, 500-, 250-, 200-, adjustable 10-100 µL capacity.

Milliliter pipettes: adjustable 0.5-5 mL capacity.

Disposable Plastic Transfer Pipettes: 1-, 5- mL.

Analytical Balance: With an accuracy of 0.0001 g.

Screw Top Bottles: 4 Oz. Nalgene (HDPE) or equivalent.

4.2 Reagents

Reagent Water: All references to reagent grade water in this method refer to deionized water. Deionized water contains no analytes above the instrumental detection limit. In this laboratory, the DI water is made from the feed of tap water passing through a mixed column system of anion and cation exchange resins. For this system, the QC criterion for DI water is ≥ 18.0 megohm-cm of electric resistance.

Nitric Acid: Baker, Trace Metal Grade or equivalent.

Nitric acid (1:1): Add 500 mL conc. Nitric acid to 400 mL of reagent grade water and dilute to 1 L.

Hydrochloric Acid: Baker, Trace Metal Grade or equivalent.

Hydrogen Peroxide (30%): Sigma, ACS Reagent Grade or equivalent.

4.3 Preparation of Spiking Solutions

Certified commercial standards are diluted to the appropriate concentration with 5% HNO_3. Table 1 provides example compositions of the spike solution used in this laboratory for the digestion of sediments. This solution can be used for either matrix spike or the laboratory blank spike.

5.0 PROCEDURES

When sediment or soil samples are received frozen, they are thawed and homogenized. To the extent possible, homogenization is performed in the original sample containers. A subsample is removed for percent dry weight and required trace element analyses. The original sample container is resealed and refrozen. After the subsamples are freeze-dried, the analytical samples are transferred to the trace metals laboratory to be homogenized using a mortar and pestle

If the original sample is small, the entire sample will be freeze-dried and then homogenized using a mortar and pestle.

If the original soil or sediment sample contains a great amount of free liquid, the liquid may be aspirated or decanted off the top of the sample. If requested, the liquid can be digested

and analyzed separately as an aqueous sample. The data should be reported separately, since the preparation for aqueous samples may not result in total trace elements because of the potential for incomplete digestion (particulate or fines present) when preparing aqueous samples.

5.1 The Sample Transfer Form is prepared and receipt of the prepared samples is documented. The sample identifications and related QC sample identification for a digestion QC batch are logged into the appropriate logbook bench sheet and the freeze-dried sample is ground prior to digestion. The sample weight is also documented on this sheet, along with any comments regarding digestion activities.

5.2 Digestion and Extraction

5.2.1 Turn on the hot plate, set the temperature to 95°C, and warm it up until it reaches that temperature. The hot plate should be located in a fume hood.

5.2.2 Approximately 1.00 g of dry powdered sediment is weighed to the nearest 0.1 mg and placed in a Pyrex beaker with a watch glass cover. The appropriate amount of spiking solution is added to beakers designated for the MS or LBS QC samples before acid digestion.

5.2.3 All acid addition and venting activities are performed in the hood. Carefully add 10.0 mL of 1:1 HNO_3 and cover the lip of beaker with a watch glass. The beaker is placed on the hot plate at 95°C for 10 minutes without boiling.

5.2.4 Beakers are removed from the hot plate and allowed to cool before 5.0 mL of concentrated HNO_3 are added. The watch glass is replaced. The beaker is returned on the hot plate, and heated at a gentle reflux for 30 minutes. Care should be taken to avoid the vigorous boiling of the solution, and to keep the volume not less than 5 mL.

5.2.5 Beakers are removed from the hot plate and allowed to cool before 2 mL of deionized water are added. Then 3 ml of 30% H_2O_2 are added using a milliliter pipette. Replace the watch glass. The beaker is returned to hot plate for the dissolution of organically bound trace metals. Continue to add 30% H_2O_2 in 1-mL aliquots for further digestion. No more than 10 mL of 30% H_2O_2 should be added during the entire digestion procedure.

5.2.6 The beakers are allowed to heat and reflux until the total volume has been reduced to approximately 4 to 5 mL or heated at 95°C ± 5°C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

5.2.7 Remove the beaker from the hot plate, and allow the beaker to cool. Then 10 mL of reagent water is added, and warmed up for several minutes, but no longer than 10 minutes.

5.2.8 Remove the beaker from the hot plate, and allow the beaker to cool. The digestates is carefully transferred to a volumetric flask, diluted to volume with reagent water, stoppered and mixed.

5.2.9 Centrifugation, standing overnight, or filtration may be chosen to separate the insoluble materials according to the requirements of clients. The separation technique should be noted in the digestion logbook.

5.2.9.1 Filtration - Filter through Whatman No. 40 filter paper (or equivalent). To control the levels of trace element contaminants in sample solutions, a HNO_3 rinsed filter paper should be used.

5.2.9.2 Centrifugation - Centrifuging the digestate at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

5.2.10 The solution is transferred from the volumetric flasks to 4 ounce. Nalgene (HDPE) sample bottles. The digestates are ready to be analyzed using the appropriate analytical SOPs for the techniques required.

5.3 Some elements such as antimony, barium, chromium, silver, vanadium, zinc, and high levels of aluminum and iron may not be completely extractable in the nitric acid. In order to obtain the reliable information on total recoverable amount of these elements, the mixture of nitric acid and hydrochloric acid may be required during the digestion. This may limit the choice of techniques for the analysis of trace metals, or may require special methods to deal with the chloride in the sample extracts.

5.3.1 Add 10 mL 1:1 HCl to the sample digest from step 5.2.6 and cover with a watch glass. Place the digestate on the heating source and reflux at 95°C ± 5°C for 15 minutes.

5.3.2 After cooling, filter the digestate through Whatman No. 40 filter paper (or equivalent). To control the levels of trace element contaminants in sample solutions, a HNO_3 rinsed filter paper should be used. Collect filtrate in a 100-mL volumetric flask. Wash the filter paper, while still in the funnel, with no more than 5 mL of hot (~95°C) 1:1 HCl, then with 20 mL of hot (~95°C) reagent water. Collect washings in the same 100-mL volumetric flask. Allow filtrate to cool, then dilute to volume.

5.3.2.1 High concentrations of metal salts with temperature-sensitive solubility can result in the formation of precipitates upon cooling

of the primary and/or secondary filtrates. If precipitation occurs in the flask upon cooling, **DO NOT** dilute to volume.

5.3.3 If a precipitate forms on the bottom of a flask, add up to 10 mL of concentrated HCl to dissolve the precipitate. After precipitate is dissolved, dilute to volume with reagent water. The solution is transferred from the volumetric flasks to 4 ounce Nalgene (HDPE) sample bottles. Samples are ready to be analyzed using the ICP instrument and the appropriate analytical SOP.

6.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

Pollution prevention contains all kinds of technique that reduces or eliminates the quantity or toxicity of waste at any point of generation. Whenever feasible, laboratory personnel should use pollution prevention technique to address the waste generation. For information about pollution prevention, please refer to *Less is better: Laboratory Chemical Management for Waste Reduction,* available from the American Chemical Society.

Laboratory waste management practices should be conducted consistent with all applicable federal and State rules and regulations to protect air, water and land. For more information on waste management, please refer to *The Waste Management Manual for Laboratory Personnel*, available from The American Chemical Society.

7.0 DOCUMENTATION REQUIREMENTS

Prior to initiating sediment or soil sample digestion activities, the folder containing the Project Initiation Form and associated paperwork should be received in the laboratory. Other copies required in this folder at the completion of digestion include:

- Sample Transfer Form
- Dry Weight Bench sheet
- The printout of calculated % Dry Weight
- A copy of the digestion logbook page (Fig.1)
- A copy of any applicable Sample Analysis Request Forms (Fig.2)

8.0 REPORTING AND PERFORMANCE

8.1 Reporting units for trace metals are µg/g, on a dry weight basis. Results may be reported as ng/g units or on a wet weight basis if requested.

8.2 Trace element performance standards are discussed in the appropriate SOP for trace metal analysis.

Table 1. Example Spike Constituents for Digestion of Sediments

Analyte	Concentration (mg/L)
Mn	250
Zn	200
B, Sr	100
Ba, Cu, Mo, Se, V	50
Ni	20
Cr	25
As, Be, Pb	10
Cd	5

Note: Add 1mL of multielement spike solution per 1g of a sample. Separate 1 mL solutions of Al, Fe and Mg at 1000 mg/L each may be added if requested by the client.

GERG Metals Digestion Log - Sediments **SD - 0191**

Client/Project: _____

SDG#: _____

Analytes: _____

Spike Sol'n & Amount: _____

#	GERG ID	Client ID	Samp Wt (g)	Comments
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				
21				
22				
23				
24				
25				
26				

	Date	Initials
Sample Prep		
Spike Added		
Spike Witness		
1:1 nitric* 10 min reflux		
Conc. nitric + 30 min. reflux		
H2O2 & 30% H2O2		
7 (1) HCl H2O2 & 10 min reflux		
Brought to Final Volume		

Circle one of the following:

☐ ICP Digestion

☐ GFAAS Digestion

* No HCL added for GFAAS digestion.

Final Volume:

Additional Comments: _____

Figure 1. Example of Sediment Digestion Bench Sheet

TEXAS A&M UNIVERSITY
Geochemical & Environmental Research Group
College of Geosciences & Maritime Studies

Inorganic Analysis Request Form

Lab SDG #:		# Samples:		Matrix:
GERG Project #:		Request Date:		
Client:		Project Manager:		Due:
Client Project Name:				

Metals

Digestion Method	Complete	Flame AA	
Total Recoverable	Closed Bomb		
Mercury Analysis	Cold Vapor	Graphite Furnace	
Other			
		ICP	

Miscellaneous

Grain Size		TOC/TIC	
GERG QC: DUP per 20 samples		GERG QC: Blank, SRM, Dup per 10 samples	
Acid Volatile Sulfides		Cyanide	
GERG QC: DUP per 20 samples		GERG QC: Blank, Dup, LCS (digested) per 20 samples	
Total Volatile Sulfides		Other	
GERG QC: DUP per 20 samples			

QA/QC Requirements

Client-Added QC: ☐ MS ☐ MSD ☐ Special SRM ☐ LBS ☐ LBSD ☐ Blank ☐ DUP ID: ____ per ____ Samples

Special Instructions:

Original: Project Files
cc: Project Manager
cc: Guy Denoux

Cc: ____
Cc: ____
Cc: Sample Custodian

Authorization Signature

Figure 2. Example of the Inorganic Analysis Request Form

This page intentionally left blank.

Appendix H

STANDARD OPERATING PROCEDURE FOR TRACE METAL ANALYSIS USING INDUCTIVELY COUPLED PLASMA (ICP) MASS SPECTROSCOPY

1.0 PURPOSE

The purpose of this document is to provide the procedures used by the staff of the Geochemical and Environmental Research Group (GERG) of the College of Geosciences at Texas A&M University for the analysis of trace metals using Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS).

This SOP describes the multi-elemental determination of analytes by ICP-MS. The method determines ions produced by a radio frequency inductively coupled plasma. Analytes of target elements originating from a liquid are nebulized to an aerosol, which is transported by argon gas into the plasma torch. The ions produced in the plasma, are introduced into a mass spectrometer by means of an interface, and then sorted according to the mass-to-charge ratios and quantified with a channel electron multiplier.

1.1 Instrumentation

The ICP-MS techniques described in this SOP are applicable for Perkin-Elmer SCIEX ELAN DRC (II) Inductively Coupled Plasma - Mass Spectrometer or the equivalents.

1.2 Applicability

These ICP-MS instrumental procedures are used for the analysis of trace metals in digestates resulting from preparation of aqueous, sediment, and biological samples.

1.3 Target Analytes and Criteria

1.3.1 The routine trace metals quantitatively determined by this method, with their recommended isotopes, are provided in Table 1.

1.3.2 The following analytes can also be determined quantitatively using the procedures described in this SOP:

Bi, Ce, Dy, Er, Eu, Gd, Ga, La, Lu, Nd, Sm,, Tm, Yb, Au, Hf, Ir, Nb, Pd, Pt, Re, Ru, Ta, Te, Zr, W, Os, and Pr. It is the responsibility of the analyst to demonstrate the accuracy and precision of the method in the sample matrix to be analyzed.

1.4 Detection Limits and Reporting Levels

1.4.1 Instrument Detection Limits (IDLs)

Because it is extremely difficult to find a "clean" matrix free of trace metals, Instrument Detection Limits (IDLs) are routinely used for ICP-MS analyses instead of method detection limits. The IDL is established by performing seven consecutive measurements each day using a standard solution at a concentration three to five times the estimated IDL. These measurements are performed on three non-consecutive days and the resulting average standard deviation is multiplied by three to determine the IDL. If multiple instruments are used, an IDL is determined for each instrument. The IDL is determined quarterly and the highest IDL is used during that quarter for reporting all data from all ICP-MSs. The IDL represents the minimum concentration of an element that can be measured and reported with 99% confidence that the element concentration is greater than zero.

1.4.2 Method Detection Limits (MDLs)

The Method Detection Limit (MDL) is defined as the minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. MDLs are determined by the preparation, digestion, and analysis of a "clean" sample matrix, either spiked with or containing the target analytes, following the procedures required by 40 CRF, Part 160, Appendix B.

1.4.3 Contract Required Detection Levels (CRDL)

Use of specific MDLs as reporting levels may be required by a contract (CRDL). Actual MDLs may be determined and used for data reporting for certain elements in a tissue or sediment matrix if requested by the client. CRDLs and the Minimum Levels (MLs) required for data reported using EPA Method 1620 in each of the typical matrices are provided in Tables 2.1 and 2.2.

1.5 Applicable Concentration Range

The composition of the routine analytical standards used for instrument calibration is determined by target analytes at the requests of clients. Calibrations have been determined to be linear over the range of standards used. Quarterly linear range studies prove that the linearity of the instrumental determinations extends beyond the high calibration standards for most elements. When sample concentrations exceed the linear range, the sample is diluted and re-analyzed.

1.6 Interferences

1.6.1 Isobaric Elemental Interferences

Isobaric Elemental Interferences are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used for correction, which involves determining the signal for another isotope of the interesting element and subtracting the appropriate signal from the analyte isotope signal. For example, tin and cadmium both have isotopes at mass 114. if cadmium is to be measured at mass 114 at the presence of tin, a correction must be made for the amount of tin presented at mass 114. This is usually done by measuring the amount of tin at an alternate isotope (e.g. Sn 118) and using the known natural abundance to correct for the amount of Sn at mass 114.

1.6.2 Isobaric Molecular and Doubly-charged Ion Interferences

They are caused by ions consisting of more than one atom or charge, respectively. Most common are the species formed in plasma with chlorides and oxides. Examples include $ArCl^+$ ions on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. Most isobaric interferences have been identified in the literature (May and Wiedmeyer, 1998). Correction equations are commonly used to deal with this kind of interference using the natural isotopes abundances for coefficient approximation. For example,

Corrected arsenic signal = (m/z 75 signal) – 3.127 * (^{77}Se - 0.815 * ^{82}Se)

Where 3.127 is the ratio of ^{35}Cl natural abundances (75.77%) to that of ^{37}Cl abundance (24.23%).

This kind of correction, however, could be problematic. In the above equation, arsenic values can be biased high when the net signal at m/z 82 is caused by ions other than $^{82}Se^+$, such as $^{81}BrH^+$ from bromine wastes.

ELAN DRC II uses chemical resolution to eliminate plasma-based polyatomic species before they reach the quadrupole mass spectrometer. This ion-molecule chemistry uses a gas to "chemically scrub" polyatomic or isobaric species from the ion beam before they enter the analyzer, resulting in improved detection limits for such elements as Fe, Ca, K, Mg, As, Se, Cr, and V.

1.6.3 Physical Interferences

Physical interferences usually result from the sample transportation and nebulization as well as the ion-transmission efficiencies. The sample transportation and nebulization can be affected if a matrix component causes a change in surface tension or viscosity.

Dissolved solids can deposit on the nebulizer tip and on the interfacial skimmer cones that reduces the orifice size and the instrument performance. TDS levels below 0.2% (2000 mg/L) is recommended to minimize the solid deposition for Elan DRC (II) ICP-MS spectrometer. Samples with high dissolved solids may require dilution prior to analysis. If the estimated amount of total dissolved material in a diluted sample is higher than 1000 ppm, the matrix matching techniques should be used.

An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that two elements are similarly affected by matrix changes. When the intensity of the internal standard is < 30% or > 120% of the intensity for the first standard used during calibration, the sample must be reanalyzed after a five fold or greater dilution.

1.6.4 Memory Interferences

It can occur when there is large concentration difference between samples or standards analyzed sequentially. Sample depositions on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences. The extended rinse period between samples or the uses of special rinse solutions usually eliminate the memory interferences.

1.7 Special Precautions

Since the instrument uses a high voltage power supply, special precautions should be taken to avoid potential danger while servicing the instrument.

2.0 GENERAL SAFETY

The hazards, toxicity or carcinogenicity of each compound or reagent used in GERG's standard operating procedures have not been precisely determined. However, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. The laboratory maintains Material Safety Data Sheets (MSDS) that contain information regarding the safe handling of chemicals used at GERG's facilities. A reference file of MSDS is available to all personnel involved with these materials. All laboratory personnel should direct any questions regarding safety issues to their supervisors or the Safety Officer.

3.0 QUALITY CONTROL

Method specific quality control (QC) acceptance criteria based on EPA Method 1620 are included in Table 3. The following QC criteria apply to routine analytical activities.

3.1 Instrument QC Criteria

3.1.1 Performing X-Y Adjustment

An X-Y adjustment should be performed after the instrument has warmed up at least 30 minutes and prior to sample analysis. Adjustments on the X and Y axes positions the cones with the plasma and aligns the instruments ion path. Peaking should be performed using a manganese solution of 1 µg/L ppm. Consult the ICP manual to correct the problem.

3.1.2 Daily Instrument QC

Prior to sample analysis, a daily instrument QC test is performed to ensure that the instrument, particularly the sample introduction components, is operating correctly. Performance is determined by evaluating the reproducibility of a daily QC solution, which has been analyzed five consecutive times. The relative standard deviation (RSD) calculated by the instrument software for each analyte should be ≤1%. If the RSD exceeds this QC acceptance criterion, corrective action should be taken. The daily QC data should be stored in the file for Daily QC runs. The oxides and doubly charged species should be ≤ 3% (see 5.3.5 and 5.3.7).

3.2 Calibration Criteria

3.2.1 Initial Calibration

3.2.1.1 A 4-point calibration curve, using background correction, is used in this procedure. The ICP-MS is linear over a wide concentration range. The ICP-MS software uses a weighted linear least-square fit for low-level determinations which permits low concentrations to have more of an impact on the fit of calibration line.

3.2.1.2 The correlation coefficient (r) should be ≥0.9950 for each analyte in the calibration curve.

3.2.1.3 The absolute value of the concentration for an element in the calibration blank should be less than the ML or CRDL for each element in question.

3.2.1.4 The RSD for three replicates at 10 ppb level should be ≤1% and at 1 ppb the RSD should be ≤5% for most elements. Significantly worse precision may be due to: inadequate uptake

time; exhausting the standard; sample introduction problems; solution chemistry; or wavelength alignment.

3.2.1.5 The initial calibration data together with the printout of the Accepted Values screen should be stored in the appropriate ICP-MS calibration file.

3.2.2 Calibration Verification

3.2.2.1 Initial Calibration Blank (ICB)

A blank (ICB) is run after each calibration and/or at the beginning of each analytical set. If the absolute calculated value for any analyte is higher than the Contract Required Detection Limit (CRDL) or the ML, corrective action should be taken. Corrective action may include a calibration update, instrumental maintenance and/or recalibration.

3.2.2.2 Continuing Calibration Blank (CCB)

A blank (CCB) is run after each 10 samples or after each 2 hours (whichever is sooner) and at the completion of each analytical set. If the absolute calculated value for any analyte is higher than the CRDL or the ML, corrective action should be taken. Corrective action may include terminating analysis, a calibration update, instrument maintenance and/or recalibration.

3.2.2.3 Initial Calibration Verification (ICV)

A low or mid-level standard (ICV) is run after calibration and/or at the beginning of each set. The QC acceptance criteria required for each analyte is a concentration determination of 90 to 110% of the true value. If any analyte value is outside of the acceptance criteria, corrective action should be taken, which may include a calibration update, instrument maintenance and/or recalibration.

3.2.2.4 Continuing Calibration Verification (CCV)

A mid-level standard (CCV) is run after each 10 samples or after each 2 hours (whichever is sooner) and at the completion of each analytical set. The QC acceptance criteria required for each analyte is a concentration determination of 90 to 110% of the true value. If any analyte value is outside of the QC acceptance criteria, corrective action should be taken, which may include terminating analysis, a calibration update, instrumental maintenance and/or recalibration.

3.3 Criteria for QC Samples for an Analytical Batch

All data from QC samples are evaluated for a specific digestion batch and analytical sequence before making decisions regarding corrective actions. However, contamination of the method blank normally requires complete redigestion and analysis of the batch, unless the concentration in all samples is 10 times that determined in the blank.

3.3.1 Method Blank

3.3.1.1 A Method Blank is used to demonstrate that the sample preparation, digestion, and analytical procedure is free of contamination. A method blank is required for each set of 20 or fewer samples in a preparation/digestion batch.

3.3.1.2 The QC acceptance criteria for the method blank specifies that if the target analytes are present in concentrations > 2 times the CRDL or ML, the preparation/digestion batch requires re-digestion, unless the concentration in a sample is 10 times higher than that found in the method blank.

3.3.1.3 Analyst discretion is used when contamination is present which does not adversely affect the overall analytical effort.

3.3.2 Duplicates

3.3.2.1 A sample Duplicate (DUP) is used to evaluate matrix homogeneity and analytical precision in the presence of a representative matrix, and is required with each set of 20 or fewer samples.

3.3.2.2 The QC acceptance criteria for duplicate analyses are that the Relative Percent Difference (RPD) between the original and its duplicate should not exceed 20%. The DUP QC acceptance criteria are advisory only and exceedance may not require re-digestion of the entire analytical batch. However, if more than two analytes are outside the QC acceptance criteria, corrective action is indicated. Corrective action may include reanalysis of the DUP and the original sample, instrument maintenance and/or recalibration, or re-digestion of the original sample and its duplicate.

3.3.2.3 The RPD is considered invalid and is not evaluated when results are less the 10 times the ML or CRDL.

3.3.3 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

3.3.3.1 A Matrix Spike (MS) sample is used to evaluate analytical accuracy in the presence of a representative matrix, and is required with each set of 20 or fewer samples.

3.3.3.2 A Matrix Spike Duplicate (MSD) is used to evaluate both analytical accuracy and precision in the presence of a representative matrix, and may be required with each set of 20 or fewer samples.

3.3.3.3 The QC acceptance criteria for analytes in the MS and MSD are a recovery of 75 to 125% of the spiked amount.

3.3.3.4 The QC acceptance criteria are invalid when the spike amount is not sufficient to increase the analyte concentrations in the sample by at least 50% (or more, as the contract requires).

3.3.3.5 If a Matrix Spike Duplicate (MSD) has been included with the analytical batch, the results obtained from the MS and MSD samples should agree within a Relative Percent Different (RPD) of 20%.

3.3.3.6 The MS and MSD QC acceptance criteria are advisory only and exceedance does not require re-digestion of the entire analytical batch. However, if more than two analytes are outside the acceptance criteria, corrective action is indicated. Corrective action may include reanalysis of the original sample and its MS/MSD, instrument maintenance and/or recalibration or re-digestion of the original sample, and its MS/MSD.

3.3.4 Standard Reference Material (SRM)

3.3.4.1 When available, a Standard Reference Material (SRM) is used to evaluate analytical accuracy for a certified reference matrix from an independent source, and is required with each set of 20 or fewer samples.

3.3.4.2 The QC acceptance criteria for measured analyte concentrations in SRM are 80 to 120% recovery of the laboratory average or the certified concentration.

3.3.4.3 This QC acceptance criteria do not apply to incomplete digestion, such as the sediment digestion required for draft EPA Method 1620.

3.3.4.4 The QC acceptance criteria are invalid when the certified analyte concentration falls below the CRDL or ML listed in Tables 2.1 and 2.2.

3.3.4.5 The SRM acceptance criteria are advisory only and exceeding the QC acceptance criteria does not require re-digestion of the entire analytical batch. However, if more than two analytes are outside the acceptance criteria, corrective action is indicated. Corrective action may include reanalysis of the SRM, instrument maintenance and/or recalibration or re-digestion.

3.3.5 Laboratory Blank Spike (LBS)

3.3.5.1 In the absence of an SRM, a Laboratory Blank Spike (LBS) may be used to evaluate analytical accuracy of the method, and may be required with each set of 20 or fewer samples.

3.3.5.2 The QC acceptance criteria for the LBS analyte recoveries is 80 to 120% of spiked amount.

3.3.5.3 If more than two analytes are outside the acceptance criteria, corrective action is indicated. After evaluation of other QC samples, corrective action may include reanalysis of the LBS, instrument maintenance and/or recalibration or re-digestion of the entire batch.

3.3.6 Post-Digestion Spike

3.3.6.1 When adequate digestate is available, a post-digestion spike may be used to demonstrate matrix effects on the sample or on the introduction system, and may be required with each digestion set.

3.3.6.2 The QC acceptance criteria for analyte recoveries in the IS are 90 to 110% of the spiked amount.

3.3.6.3 The IS acceptance criteria are advisory only. However, if more than two analytes are outside the QC acceptance criteria, corrective action may be indicated. Corrective action may include dilution, use of serial dilutions, or redigestion of the entire analytical batch.

4.0 OPERATING CONDITIONS

4.1 ICP Source

The PerkinElmer SCIEX Elan DRC II ICP-MS instrument uses hot argon plasma to serve as an excitation source. This is produced by a 40.44 MHz free-running oscillator that can operate at any ICP-MS power level up to 2.0 KW.

4.2 Argon Supply

The quartz ICP-MS torch has three concentric tubes, each carrying a flow of argon. The outer tube carries the **Plasma Gas** flow, which acts as a barrier between the quartz and the extremely hot plasma. The plasma gas also provides the argon for the plasma itself. The central tube carries the **Auxiliary** gas flow, and the inner injector tube carries the sample aerosol in the **Nebulizer** gas flow. High purity grade or better grade of argon (99.99%) is recommended for Elan DRC II ICP-MS spectrometer. The argon supply pressure should be within the range of 50 ± 1 psi.

4.3 Operating Parameters

Four operating parameters are used to control the hot argon plasma's condition: generator power, plasma gas flow, auxiliary gas flow, and nebulizer gas flow. In addition, the delivery rates of the peristaltic pump for sample solutions and internal standards are also critical to analytical performance. All these operating parameters vary according to the analytical procedure. Specific criteria should be stored under each analytical method name in the ICP-MS software. Hard copies of the analytical method screens are maintained in the trace metals laboratory office file. Typical operating parameters for the Modified Scott Spray Chamber used for this operating procedure are shown in Table 4.

5.0 INSTRUMENT SET-UP PROCEDURE

5.1 Before ignition:

Check pump tubing and replace if worn
Check sample tubing and drain tubing in good condition

1.1.1.1 Verify and if necessary adjust pump tension

Verify and if necessary clean the skimmer and sampler cones
Verify and if necessary adjust torch alignment

1.1.1.1.1.1.1 Verify and if necessary clean the load coil

Check nebulizer operation before turning on the plasma

1.1.1.2 Turn on the gases and cooling system

Check the vacuum pressure, in the 10^{-6} torr range.

1.1.1.3 Ensure the ELAN software is running

5.2 After ignition:

Warm up the instrument for at least 30 minutes before performing analysis.

Daily QC procedures must be performed after proper warm up time to ensure that the instrument, particularly the sample introduction components, is operating correctly.

1.1.1.3.1 5.3 Instrument Optimization

These following steps of optimization are specifically for the Elan DRC II ICP-MS spectrometer. For other ICP-MS spectrometers, please consult the appropriate instrument and software manuals. Bold text defines specific selections in the operation software.

5.3.1 Performing Mass Calibration

A solution of 1 µg/L of Mg, In, Pb, Ce, and Th in 0.5% HNO_3 and **Tuning.wrk** are used to perform the mass calibration. Click **Tune Mass Spec** in the tuning window to perform a full AutoTune. The measured mass for C, Mg, Ar_2, In, Ce, Pb, and Th should be within the actual mass values ± 0.05 amu. If any value is outside the range, do tuning mass again. Repeat this step until the values are within range. After tuning measurement, place the sample capillary into deionized water to flush the system.

5.3.2 Performing X-Y Adjustments

Open the **Performing X-Y Adjustment.wrk** workspace. Aspirate a solution of 10 µg/L of Mg, In, and Pb in 1% HNO_3. In the sample window,

click **Analyze Sample**. Open the Realtime graphics window, and add In to the analyte list, and adjust the X (Horizontal, closer to interface) and Y (Vertical, closer to operator) knobs under the top cover of instrument. Set the knobs at the position resulting in maximum signal intensity. You should always perform the Y adjustment first.

5.3.3 Optimizing Nebulizer Gas flow for Maximum Intensity

Open the **Optimizing Nebulizer Gas Flow.wrk** workspace. In the optimization window, click **Auto Optimize** tab and then click **ICP RF Power** in the parameter description list box. In the **Current Value** field, type the typical value (1200 W). Then click **Nebulizer Gas Flow** in the parameter description list box. Click **Get Analyte List** and make sure that **In 114.904** appears in the **Analyte** field. Choose the **Maximum Intensity** option in the optimization criteria group, and click **Get Defaults**. Aspirate a solution of 1 µg/L of Mg, In, Ce and U in 1% HNO_3 and click **Optimize**. Ensure that a good optimization curve is obtained (like a mountain). Save the optimization file.

5.3.4 Optimizing the Auto Lens Voltage

Open the **Optimizing Autolens.wrk** workspace. In the optimization window, click **Auto lens** tab and click **Clear Calibration**. Click **OK** to confirm. Click to get the default analyte list (Be, Co, and In). Aspirate a solution of 1 µg/L of Be, Co, and In in 1% HNO_3 and click **Calibrate** in the **Auto Lens** tab. Ensure that a good plot of lens voltage vs. mass is obtained (linear line). Save the optimization file.

5.3.5 Optimizing Nebulizer Gas Flow for 3% Oxides

Open the **Optimizing Nebulizer Gas Flow.wrk** workspace. In the optimization window, click **Auto Optimize** tab and then click **ICP RF Power** in the parameter description list box. In the **Current Value** field, type the typical value (1200 W). Then click **Nebulizer Gas Flow** in the parameter description list box. Click **Get Analyte List and Get Defaults**. Choose the **Formula** option in the optimization criteria group, and fill in the formula in drop-down menu box with the following expression: CeO 156 /Ce 140 < 0.03. Aspirate a solution of 1 µg/L of Mg, In, Ce and U in 1% HNO_3 and click **Optimize**. Save the optimization file.

5.3.6 Cross Calibrating the Dual Detector

Open the **Dual detector Calib.wrk** workspace. In the optimization window, click **Dual Detector Calibration** tab. Click **Get Analyte List**, and in the lens voltage group, set the **Start Value** to -3 and the **End Value** to 15 and the **Step Value** to 0.25. Aspirate a solution of 200 µg/L of Mg, Cu, Rh and Pb in 1% HNO_3 (add other analytes as necessary in a specified analysis) and click **Calibrate**. In the interactive graphics window, a plot of intensity vs. mass displays. Save the optimization file.

5.3.7 Checking Instrument Performance

A solution of 1 μg/L of Mg, In, Rh, Ce, Ba and U in 1% HNO_3 and the workspace of **Daily Perfomance.wrk** are used to check the instrument daily performance. Click **Analyze Sample** in the sample window of the workspace. The instrument must be on at least 30 min with the plasma on before the optimization will be performed. Typical performance specifications are:

Sensitivity:

Mg > 8,000 cps

In, Rh > 40,000 cps

Background:

220 < 2 cps

Doubly charged and oxides:

Ba++/Ba < .03

CeO/Ce < .03

If performance check is satisfactory, it is ready to begin the analysis. Place the sample capillary into deionized water to flush the system. If not satisfactory, the nebulizer gas flow and RF power need to be optimized for 3% oxides and doubly charged species. Calibrate the auto lens, and then recheck the system.

6.0 ANALYTICAL STANDARDS

Analytical standards are purchased or prepared as solutions. Standards are stored in plastic containers (HDPE or LDPE Nalgene) at ambient temperature. Purchased standards are certified to ensure their purity, concentration, and authenticity. Prepared standards must meet the following QC acceptance criteria.

All target analytes should be present at ± 5% of the expected concentrations. For calibration verification, analysis of an EPA or NIST-traceable analytical standard using the new calibration standards should meet all QC acceptance criteria.

6.1 Instrument Calibration Standards

A four (4)-point calibration curve is used for most trace metal analyses by ICP-MS. Standard 4 (S4) is the highest concentration solution (usually 200 µg/L), Standard 1 (S1) is the blank, and Standards 2 and 3 (S2 and S3) are intermediate standard concentrations (1 and 20 µg/L, respectively). For silver, the concentrations may be reduced to half of the corresponding values. After the ICP-MS is calibrated, the calibration curve is evaluated using the analysis of initial and continuing calibration blanks and standards (see Sections 3.2 and 6.4).

6.1.1 Calibration standards are either purchased as custom multi-element solutions or prepared in-house from purchased single element solutions at the desired concentrations.

6.1.2 As required, calibrations standards are diluted using the appropriate Class A volumetrics and/or calibrated pipettors with a 0.5% or 1% nitric acid solution, depending on the analytical procedure being used.

6.2 Spiking Solutions

Spiking solutions are prepared for each matrix. Standards are prepared in 5% nitric acid using the appropriate Class A volumetric glassware and/or calibrated pipettors. Samples (and LBS when required) are spiked with the appropriate spiking solution at a minimum of 1 per 20 or fewer samples for each digestion batch. Matrix spike composition for sediments and tissues are listed in Tables 5-1 and 5-2, respectively.

Waters are spiked with the elements listed in Table 5-2 using 500 µL for each prepared 50 mL water sample.

6.3 Daily Instrument QC Solution

6.3.1 Using Class A volumetric glassware, a daily QC solution is prepared using single element stock solutions for a final concentration of 1 µg/L Al, Cr, Mn, Cd, Cu, Ba, Th, Pb, In, Rh, Mg, Ce, and U in a 1% nitric acid matrix. The Daily Instrument QC solution is analyzed once every 24 hours or whenever the instrument is set-up.

6.3.2 This solution can also be used for performing mass calibration, optimizing nebulizer gas flow for maximum intensity, and optimizing nebulizer gas flow for 3% oxides.

6.4 Internal Standard Solutions

The most common internal standard elements for ICP-MS are listed in Table 6. Using Class A volumetric glassware, an internal standard solution is prepared using single element stock solutions or commercially available mix internal standard for a final concentration of 10 µg/L Li, Bi, Ho, In, Rh, Sc, Tb, and Y in a 1% nitric acid matrix. The internal standard solution is analyzed at the same time when calibration standards and samples are analyzed. It is pumped into the nebulizer by a separate pump at a speed 10 times slower than the sample pump rate.

6.5 Auto Lens Calibrating Solution

Using Class A volumetric glassware, an auto lens calibrating solution is prepared using single element stock solutions for a final concentration of 1 µg/L Be, In and Co in a 1% nitric acid matrix.

6.6 X-Y Adjustment Solution

Using Class A volumetric glassware, an X-Y adjustment solution is prepared using single element stock solutions for a final concentration of 1 µg/L Mg, In, and Pb in a 1% nitric acid matrix.

6.7 Calibrating Dual Detector Solution

Using Class A volumetric glassware, a solution for calibrating the dual detector is prepared using single element stock solutions for a final concentration of 200 µg/L of Mg, Cu, Rh and Pb in 1% HNO_3 (add other analytes as necessary for a specified analysis). The highest calibration standard solution can also be used as dual detector calibrating solution.

6.8 Independent Continuing Calibration Verification Solution

6.8.1 A continuing calibration blank standard (CCB, usually just diluted acid such as 1% HNO_3) is analyzed every 10 samples or every 2 hours, prior to the calibration verification standard (CCV).

6.8.2 A continuing calibration verification standard (CCV) is analyzed every 10 samples or 2 hours. This sample is prepared in a same way as Calibration standard 3 (S3), but from different sources in 1% nitric acid to the appropriate concentration(s). Single element stock solutions may also be

diluted in 1% nitric acid to the appropriate concentrations for this check standard.

6.9 Instrument Spike Solution

One sample (sediment or water) per digestion batch is spiked with this solution at the instrument. For a tissue digestion, this solution is diluted with 1% nitric acid and analyzed as a blank spike or calibration spike.

6.10 Standard Reference Material (SRM)

When available, a NIST, NRCC or NIST/NRCC-traceable SRM is analyzed with each digestion batch to evaluate both digestion procedures and instrument performance. The SRM is matrix matched to the matrix being digested.

7.0 REQUIRED SAMPLE DOCUMENTATION AND IDENTIFICATION

Copies of the following documents (as appropriate for the sample types) must be kept for each sample set in a labeled folder in the trace metals laboratory office.

7.1 Chain of custody documents

7.2 Sample information sheet

7.3 Inorganic Analysis Request Form (See SOP 9802)

7.4 Laboratory Digestion Bench sheet (See SOP 9802)

7.5 Dry Weight Bench Sheet

8.0 SAMPLE ANALYSIS

8.1. Choose the analytical method from the ICP-MS software according to the sample matrix type and required analyte list. See the examples of the methods in the ICP–MS software or review the hard copy maintained in the trace metals laboratory office.

8.2. Set appropriate rinse and uptake time (not less than 45 seconds and 25 seconds, respectively).

8.3. Check the ICP-MS calibration as described in 3.2.

8.4. Analyze samples and all related QC samples under the same conditions as standards (same integration time, background correction points, plasma conditions etc.).

8.5 After the run is completed, review the results of quality control samples for PASS/FAIL criteria. Export the data to disk in MS Excel format and report it daily using the appropriate templates.

9.0 INSTRUMENT MAINTENANCE

Table 7 provides a summary of both routine and preventive maintenance for the PerkinElmer SCIEX Elan DRC II ICP-MS. More maintenance may be required as necessary. All maintenance and repairs made to the ICP-MS are recorded in the "ICP-MS Maintenance Log".

10.0 DOCUMENTATION REQUIRED FOR ANALYTICAL RESULTS

10.1 All analytical runs are recorded in the "ICP-MS Instrument Run Log," with the analysis date, client identification, digestion page, instrument protocol, analyst initials, and any relevant comments.

10.2 All initial calibration data together with accepted values are stored in "Calibration Files".

10.3 For each analytical batch, the documents noted in Section 7 as well as the following documentation, are maintained as required by contract (or for a period not less than one year).

10.3.1 Initial and/or Continuing Calibration Verification data on raw data printout.

10.3.2 Calibration Update data on raw data printout.

10.3.3 All analytical and laboratory QC samples data on raw data printout.

References:

Thomas W. May and Ray H. Wiedmeyer, 1998, A Table of Polyatomic Interferences in ICP-MS. Atomic Spectroscopy, 19(5): 150-155.

Elan Version 2.4 Software guide for ICP mass spectrometry, available from Perkin-Elmer SCIEX Instruments, Document 1002821.

J. T. Creed, C. A. Brockhoff, and T. D. Martin, 1994 - USEPA METHOD 200.8 Determination of trace elements in waters and wastes by inductively coupled plasma – Mass Spectrometry Revision 5.4.

USEPA Method 1620, 1989. Metals by Inductively Coupled Plasma Atomic Emission Spectroscopy and Atomic Absorption Spectroscopy.

USEPA Method 6020, 1994. Inductively Coupled Plasma – Mass Spectroscopy.

Table 1. Applicable elements and recommended mass for routine ICP-MS analysis

Element	Symbol	Recommended Mass
Aluminum	Al	27
Antimony	Sb	121, **123**
Arsenic	As	75
Barium	Ba	**135**, 137
Beryllium	Be	9
Bismuth	Bi	210
Boron	B	11
Cadmium	Cd	111, **114**
Calcium	Ca	44
Chromium	Cr	**52**, 53
Cobalt	Co	59
Copper	Cu	**63**, 65
Iron	Fe	54, 56, 57
Lead	Pb	206, 207, 208
Lithium	Li	7
Magnesium	Mg	24, **25, 26**
Manganese	Mn	55
Mercury	Hg	202
Molybdenum	Mo	95, **97**, 98
Nickel	Ni	**60**, **61**, 62
Phosphorus	P	31
Potassium	K	39
Ruthenium	Ru	99
Selenium	Se	77, **82**
Silicon	Si	28
Silver	Ag	**107**, 109
Sodium	Na	23
Strontium	Sr	88
Sulfur	S	32
Thallium	Tl	203, **205**
Thorium	Th	232
Tungsten	W	184
Uranium	U	238
Tin	Sn	**118**, 120
Titanium	Ti	48
Vanadium	V	51
Yttrium	Y	88
Zinc	Zn	66

Table 2.1. Routine Contract Required Detection (CRDL) and Reporting and Levels for the U.S. Fish and Wildlife and Other Projects.

Analyte	Tissues (mg/L-Dry Weight)	Sediment (mg/L-Dry Weight)	Water (mg/L-Wet Weight
Arsenic	0.50	0.50	0.005
Selenium	0.50	1.0	0.005
Mercury	0.20	0.20	0.004
Aluminum	5.0	10.0	0.05
Boron	2.0	10.0	0.10
Barium	1.0	1.0	0.005
Beryllium	0.10	0.20	0.0005
Cadmium	0.10	0.20	0.0005
Chromium	0.50	1.0	0.003
Copper	0.50	1.0	0.005
Iron	5.0	10.0	0.10
Magnesium	5.0	10.0	0.10
Manganese	1.0	5.0	0.005
Molybdenum	2.0	5.0	0.05
Nickel	0.50	5.0	0.005
Lead	0.50	5.0	0.01
Strontium	0.50	5.0	0.001
Vanadium	0.50	1.0	0.001
Zinc	1.0	5.0	0.01

Table 2.2. Minimum Levels Required for EPA Method 1620.

ICP Analyte	ML (µg/L)	AA Analytes	ML (µg/L)
Aluminum	200	Antimony	20
Barium	200	Arsenic	10
Beryllium	5	Lead	5
Boron	100	Selenium	5
Cadmium	5	Thallium	10
Calcium	5000	Mercury	0.2
Chromium	10		
Cobalt	50		
Copper	25		
Iron	100		
Lead	50		
Magnesium	5000		
Manganese	15		
Molybdenum	10		
Nickel	40		
Silver	10		
Sodium	5000		
Tin	30		
Titanium	5		
Vanadium	50		
Yttrium	5		
Zinc	20		

Table 3. Key Elements of ICP-MS Quality Control.

Element	Control Limit Criteria	Frequency
1. Initial and Periodic Analytical Requirements		
- Instrument Detection Limit (IDL), All Instruments	Must meet Minimum Levels (MLs) specified in contract or Method 1620.	Within 30 days of start of contract analysis and quarterly during contract period or after major instrument adjustment.
- Initial Precision and Accuracy (IPAR), All Instruments	Recovery range of 75-125% for each element; %RSD meets Method 1620, Table 8 criteria.	Initial for each type of instrumental analysis, annually thereafter.
- Analysis of Performance Evaluation (PE) Samples	Minimum passing score is 75 out of 100 points.	Initial and at regular intervals throughout the year
- ICP Linear Range Verification Check Standard Analysis (LRA)	Within ± 5% of true value for quantitative ICP analytes.	For each element at each wavelength and then quarterly during contract period.
2. QC Requirements for ICP Quantitative Analysis		
- Instrument Calibration	Minimum of a blank and one standard; correlation coefficient of 0.995 or better. Baseline correction or resloping acceptable if preceded and followed by ICV/ICB or CCV/CCB.	Each time the instrument is set-up (initialized) and then each 24 hours during a continuous run.
- Initial Calibration Verification (ICV)	Within ±10% of the true value. If fails, stop, recalibrate, and reanalyze.	Immediately after system calibration and at beginning of each analysis run.
- Initial Calibration Blank (ICB)	Absolute value □ML for quantitative analyses. When fails, recalibrate, reprocess with ICV, ICB.	After every ICV.
- ICP Minimum Level Standard Solution (CRI)	Use ICP standard at 2x ML or 2x IDL, whichever is greater. Compare to MLs on Table 3.2; control limits not yet specified; report recoveries.	After ICV/ICB and at end of each analysis run or twice per 8-hour shift, whichever is more frequent. CCV, CCB must follow analysis of the CRI sample.
- Continuing Calibration Verification (CCV)	Within ±10% of the true value. If fails, stop, recalibrate, and reanalyze back to last passing CV. Same CCV must be used for entire Episode or sample set.	At a minimum of every 10% or every 2 hours during an analysis run, and after the last analytical or QC sample.

Table 3. (Cont.)

Element	Control Limit Criteria	Frequency
- Continuing Calibration Blank (CCB)	Absolute value □ML for quantitative analyses. When fails, recalibrate and reanalyze back to last acceptable CB.	After every CCV.
- Interference Check Samples for ICP (ICSA and ICSAB)	The ICSAB must be within ± 20 of the true value of the solution after consecutive runs of ICSA and ICSAB. If fails, stop, correct, recalibrate, and reanalyze back to last acceptable ICS pair.	Analyze consecutively at beginning and end of each analysis run or once every 12 hours.
- Laboratory Control Sample (LCS)[1]	Recovery within 80 - 100% (except for Ag), or if fails, terminate analysis, redigest and reanalyze. For Ag, qualify results outside 80-120% and report.	One LCS per sample set or Episode, whichever is more frequent.[2]
- Preparation Blank (PB)	Absolute value ≤ the ML; if it fails, the associated samples > ML and ≤ 10 ML must be reprocessed; samples > 10 ML can be reported.	One PB with each sample set prepared.
- ICP Digested Matrix Spike[3]	Recovery range 75% to 125%; repeat analysis if fails; then recalibrate if fails; if this continues to fail, dilute by 10, report and qualify.	At least 10% of samples analyzed per matrix per sample set.
- ICP Digested Matrix Spike Duplicate[4]	Same recovery criteria as for matrix spike. RPD □20% is acceptable range for inorganic elements; report and qualify failure.	At least 10% of samples analyzed per matrix per sample set.
- ICP Serial Dilution Analysis	If analyte is 50x IDL, the % difference must agree within 10% of original, or flag all associated data if > 10%.	On 10% of samples analyzed or at least one per sample set whichever is more frequent.

Note 1: Analysis of Standard Reference Materials (SRM) as an LCS requires a recovery ± 20% of certified values for complete digestions only.

Note 2: A sample set is a group of up to 20 field samples (20 samples or less) prepared at the same time and associated with the same QC samples.

Note 3: Samples to be spiked are normally specified by the client; matrix spike solutions contain selected analytes of interest. The spike concentration of each analyte in the solutions 1-5 x background sample level or 5-50 x MDL for non-detects.

Note 4: RPD = Relative percent difference between spike recovery results for matrix spike and matrix spike duplicate.

Table 4. Typical Perkin-Elmer Elan DRC (II) ICP-MS Spectrometer Conditions

RF Power	1200 Watts
Plasma Gas Flow	15 L/min
Auxiliary Gas Flow 1.20 L/min	
Nebulizer Gas flow	0.96 L/min
Solution Pump Rate	1.5 mL/min
Sample Introduction System	Cross-flow with concentric spray chamber
Rinse Time	45 s @20rpm
Sample Uptake Time	25 s @20rpm
Equilibration Time	20 s @20rpm
Analysis Time	dependent on the number of target analytes
Detector Mode	Dual mode (Pulse/analog)
Lens	Auto lens enabled, lens voltage 5.0 – 9.0 V
Sampler/Skimmer Cones	Nickel
Scanning Mode	Peak hopping
Number of Points/Peak 1	
Dwell Time	50 ms per point
Number of Sweeps/Reading	8
Number of Readings/replicate	1
Number of Replicates	3

Table 5-1. Matrix Spike Constituents for Sediments

Analyte	Concentration (mg/L)
Mn	250
Zn	200
B, Sr	100
Ba, Cu, Mo, Se, V	50
Ni	20
Cr	25
As, Be, Pb	10
Cd	5

* Spike amount: 1mL of multi-element spike solution per 1g of a sample for mixed analyte

Table 5-2. Matrix Spike Constituents for Tissues

Analyte	Target Concentration (mg/L)
Mg	1000
Fe	500
Al, Zn	100
B, Mn, Cu, Mo, Se	50
Sr	25
As, Cr, Ni, V	20
Ba	10
Be, Pb	5
Cd	2.5

*Spike amount: 1 mL of multi-element spike solution per 1 g of sample. Tissue spike can also be used for water digestions using 500 □L of the spike for each 50 mL water sample.

Table 6. The Most common internal standards used in ICP-MS

Analyte	Symbol	Isotopes Possible	Monitored limitation
Lithium	Li	6	a
Scandium	Sc	45	Polyatomic ion interference
Germanium	Ge	72	
Yttrium	Y	89	a, b
Rhodium	Rh	103	
Indium	In	113, **115**	Isobaric interference by Sn
Terbium	Tb	159	
Holmium	Ho	165	
Lutetium	Lu	175	
Bismuth	Bi	209	a

a May be present in environmental samples.
b Yttrium may form measurable amounts of YO^+ (105 amu) and YOH+ (106 amu), which may affect the cadmium correction equation.

Table 7. The Maintenance Schedule of ELAN DRC II ICP-MS

Frequency	Maintenance Item
Daily	
	All things described in 5.1
	Auto lens calibration
	Tubing and connectors for gas
	Nebulizer performance
	Nebulizer gas optimization
	Ion lens voltage optimization
	Torch and spray chamber performance
	Performance QC test
Weekly	
	Tubing and connectors for solution
	Pump tubing
	Sampler and skimmer cones cleaning
	Autosampler and sipper cleaning and lubrication
	Drain the mist eliminators
	X-Y peak adjustments after cones and torch box serviced
Monthly	
	Clean and conditioning Ion lens
	Change interface pump oil
	Clean or replace air filters
	Check RF contact strip for corrosion and looseness
	Oil sample introduction pump
	Quadruple Rod offset
	Check plastic connectors and parts for wear
	Check nebulizer and its adaptor O-rings
Semiannual	
	Drain water recirculator, clean it, and refill w/DI water
	Check argon line filter and replace as necessary
Annual	
	Preventive maintenance call serviced by PerkinElmer field service engineer is recommended
	The rotary pump oil for MS is changed
Biannual	
	Change backing pump oil
As needed	
Source assembly for MS is cleaned and (/or) replaced	

This page intentionally left blank.

Appendix I

Texas A&M, Geochemical and Environmental Research Group
STANDARD OPERATING PROCECURES SOP-9805
Revision No. 2
May 22, 2002
EXTRACTING SEDIMENT SAMPLES USING ACCELERATED SOLVENT EXTRACTOR FOR THE ANALYSES OF ORGANOCHLORINE PESTICIDES, POLYCHLORINATED BIPHENYLS AND AROMATIC HYDROCARBONS

1.0 PURPOSE

This document provides the procedures for the extraction of sediment samples using the Accelerated Solvent Extractor (ASE) and the subsequent concentration of the extracts for environmental trace analysis which are used by the staff of the Geochemical and Environmental Research Group (GERG) of the College of Geosciences at Texas A&M University.

1.1 Summary of the Method

This procedure uses matrix-specific extraction and analyte-specific concentration steps to allow the determination of organochlorine pesticides (OCs), polychlorinated biphenyls (PCBs), and polynuclear aromatic hydrocarbons (PAHs) in environmental samples. With modification, this method may by used for the extraction of other types of matrices and for other types of analytes.

The sediment samples are weighed and placed into extraction cells. The desired solvent is placed into the solvent reservoir of the ASE 200. The method for extraction is selected and initiated. The extract is released into collection vials. The extracts are then concentrated on a water bath. The concentrated extract is purified by column chromatography using appropriate GERG SOPs.

1.2 Application of Method

1.2.1 The extraction method described in this standard operation procedure is applicable to wet and dried sediment samples that require measurement of aliphatic hydrocarbons, OCs, PCBs, and PAHs. With modification to the extraction conditions, other types of compounds, such as herbicides, organophosphorus pesticides, and dioxin/furans from various types of matrices may be extracted by this technique.

2.0 SAFETY

The hazards, toxicity or carcinogenicity of each compound or reagent used in GERG standard operating procedures have not been precisely determined. However, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. The laboratory maintains Material Safety Data Sheets (MSDS) which contain information regarding the safe handling of chemicals used at GERG facilities. A reference file of MSDS is available to all personnel involved with these materials. All laboratory personnel should direct any questions regarding safety issues to their supervisors or the Safety Officer.

3.0 QUALITY CONTROL REQUIREMENTS

The quality control samples routinely used at GERG include a method blank (BLANK), a sample duplicate (DUP), a matrix spike (MS), and a matrix spike duplicate (MSD) per batch of 20 or less samples. The number and type of QC samples may be modified to satisfy client's requests and sample availability. A laboratory blank spike (LBS) and standard reference material (SRM) may be included in each extraction batch.

3.1 Method Blank (BLANK)

A Method Blank is used to demonstrate that the analytical method is free of contaminating interference. The BLANK is prepared by executing all of the specified extraction and extract purification steps except for the introduction of a sample. The BLANK is spiked with Surrogate Standard Solution (SU) and the Internal Standard (IS) at the appropriate stages of the preparation.

3.2 Laboratory Blank Spike (LBS)

A Laboratory Blank Spike is used to demonstrate accuracy of the method. It is prepared by executing all of the specific extraction and extraction purification steps except for the introduction of a sample. The LBS is spiked with the Surrogate Standard Solution (SU), the matrix spike standard (MA), and the Internal Standard (IS) at the appropriate stages of the preparation.

3.3 Matrix Spike (MS) and Matrix Spike Duplicate (MSD)

Matrix Spike/Matrix Spike Duplicate are used to demonstrate accuracy and precision of the sample processing method in the presence of a representative matrix. MS/MSD are prepared by executing all of the specified extraction and purification steps on a selected sample. The MS/MSD are spiked with the Surrogate Spiking Solution (SU), the Matrix Spike Standard (MA) and the Internal Standard (IS) at the appropriate stages of the preparation.

3.4 Duplicate (DUP)

A sample Duplicate is used to demonstrate matrix homogeneity and analytical precision in the presence of a representative matrix. A DUP is prepared by executing all of the specified extraction and purification steps on replicate portions of a selected sample. The DUP is spiked with the Surrogate Standard Solution (SU) and the Internal Standard (IS) at the appropriate stages of the preparation.

3.5 Standard Reference Material (SRM)

A standard reference material (SRM) is used to demonstrate the relative accuracy of the sample processing and analytical methods in the presence of a representative matrix.

4.0 APPARATUS AND MATERIALS

3.1 Glassware and Hardware

The following laboratory glassware and hardware is needed to perform the extraction and concentration procedures:

Stainless steel forceps
Flat-bottomed Flasks: 250 mL
Collection Vials and Caps: 60 mL capacity
Beakers: 50 mL
Stainless Steel Extraction Cells and Caps: 22 or 33 mL capacity, Dionex
Water Bath: Heated to 40-50° C
Balance: Top Loading, 0.001 g accuracy
Funnels
Glass Wool

4.2 Instrumentation

Accelerated Solvent Extractor: ASE 200, Dionex

5.0 REAGENTS AND CONSUMABLE MATERIALS

5.1 Reagents

5.1.1 Hydrochloric Acid: 38%; VWR Scientific, Cat. HX0603-3 or equivalent.

5.1.2 Solvents: Equivalent solvents from other source may be used after lot testing. Methylene Chloride: Burdick and Jackson; Cat# 300-4, High Purity, Pesticide grade or equivalent.
Hexane: Burdick and Jackson; Cat# GC60394-4, Capillary GC/GC-MS solvent or equivalent.

Acetone: Burdick and Jackson; Cat# 010-4, High purity solvent or equivalent.
Methanol: Burdick and Jackson; Cat# 230-4, pesticide grade or equivalent.

5.1.3 Nitrogen Gas: Compressed nitrogen

5.1.4 Sand: White quartz, Sigma, combusted at 440°C for 4 hours

5.1.5 Copper, Granular: 20-30 mesh: J.T. Baker

5.1.6 Glass Microfibre Filters; GF/B: 21mm; Whatman Cat# 1821-021, combusted at 440°C for 4 hours

5.1.7 Sodium sulfate, J. T. Baker; analytical grade, combusted at 440°C for 4 hours

5.2 Analytical Standards

Appropriate analytical standards are specified on the Analysis Request Form and are prepared according to GERG SOPs. When not in use, standards are stored at 4°C in a refrigerator.

6.0 EXTRACTION PROCEDURE

6.1 Reagent and Apparatus Preparation

6.1.1 Preparation of Activated Copper:

6.1.1.1 Pour desired amount of granular copper into a beaker. Add enough amount of diluted 1:1 hydrochloric acid to the beaker to cover the copper. The acid is diluted in the hood by slowly adding an equal volume of acid to the water with stirring. Let the copper stand in acid for approximately 2-5 minutes.

6.1.1.2 Slowly decant the acid into the acid container. Add baking soda to another beaker. Add water to the copper, stir, and decant the liquid onto the baking soda. Continue the water rinsing process until the acid is neutralized (no bubbling when added to the baking soda).

6.1.1.3 Wash the copper with methanol three times, or until the methanol wash is clear, by adding methanol into the beaker and stirring. Decant the methanol into an appropriate waste container.

6.1.1.4 Wash the copper with methylene chloride three times, or until the methylene chloride wash is clear, by adding methylene chloride to the beaker and stirring. Decant the methylene chloride into an appropriate waste container. Transfer the copper into a clean beaker and cover with hexane.

6.1.2 Clean Extraction Cell Tube

Disassemble the extraction cell by unscrewing the cap. Wash the extraction cell tube with soap and water using a brush. After rinsing with water, rinse the inside of the tube with acetone or methanol, followed by methylene chloride.

6.1.3 Clean Cell Caps

Wash the cell caps with water. Rinse the caps with methanol, followed by methylene chloride. Before assembling, carefully check the inside of the caps. Make sure there is no sand, copper, sediment, or any other residual dirt inside the cap, particularly around the brown PEEK seal. If there is any, disassemble the cap and clean it.

6.2 SAMPLE PREPARATION

6.2.1 Calibrate Balance

6.2.1.1 Tare the balance. Place a standard weight (100 g) on the weighing pan. Press CAL button. Record the weight displayed. If the weight differs from the standard by 0.005 g, re-calibrate the balance by pressing CAL button. If the reading is still out of the range of 99.995 g to 100.005 g, notify your supervisor.

6.2.2 Aliquot a 20 gram subsample into a clean jar. If the sample contains greater than 30% of water, partially dry the sample at 40°C for 3-5 hours.

6.2.3 Mix the sample with 15-20 gram anhydrous sodium sulfate. Stir the sample/sodium sulfate constantly until the mixture free flows. Assemble the 33 mL extraction cell body tube and bottom cap, hand tight. Rinse with methanol and methylene chloride.

6.2.4 Insert a combusted filter into the cell and push down with a rod. Make sure the filter is flat and covers the bottom fully.

6.2.5 Using a funnel, add one scoop of the activated copper to the extraction cell.

6.2.6 Using a funnel, add the sample/sodium sulfate mixture into the extraction cell.

6.2.7 Prepare a Blank and Spiked Blank sample (if required) by preparing a cell filled with sand along with copper and filter.

6.2.8 Rinse a micropipette with methylene chloride in the hood at least five times. Spike all samples with the appropriate amount of the required surrogate standards.

6.2.9 Rinse the micropipette five times again and spike the appropriate samples with the required amount of spiking standards.

6.2.10 Using caps that have been rinsed with methanol/methylene chloride, screw the top cap onto the cell hand tight.

6.3 Extraction

6.3.1 Place the assembled extraction cells onto the top cell tray on the ASE 200 in numerical order according to slots.

6.3.2 Place labeled 60 mL collection vials in the bottom collection tray to coincide with the top tray.

6.3.3 Fill the solvent reservoir with methylene chloride, or other solvent if specified.

6.3.4 Make sure the solvent waste/rinse collection vial inside the chamber of the reservoir is empty, as well as the rinse vial on the sample collection tray (R1, R2).

6.3.5 Press ***RINSE*** button on the control panel.

6.3.6 As the status returns to ***IDLE*** after instrumental rinse, press ***MENU*** and choose the first selection ***LOAD METHOD/ SCHEDULE*** to designate the method. Enter the desired method number, press ***ENTER***, and then press ***START.*** This will start the instrument extraction beginning with the first extraction cell.

The conditions used for the extraction of the environmental sediment are:

Temperature	100°C
Pressure	1500 psi
Heating time	5 minutes
Flush volume	90%
Cycles	2

If required, the extraction may be started from cells other than the first cell. If so desired, press ***MENU*** and choose the first selection ***LOAD METHOD/SCHEDULE*** to designate the method. Move the cursor to the third entry field and enter the vial number you wish to begin with. Move the cursor to ***METHOD NUMBER*** and enter the method number. Press ***ENTER***. Press ***START*** and the extraction process should begin.

While the extraction is in progress, check the collected solvent volume in the sample collection vial. The vial should be more than half-full for the 33 mL extraction tubes. Check for leaking cells by listening to the pump action. If the pump is continuously activated while the machine is in ***STATIC***, or if the pressure reading is constantly below the setting (1500 psi) then there is probably a leak. If this occurs, stop the extraction by pressing the ***ABORT*** button on the control panel.

6.4 Concentration

6.4.1 Filter the sample extract by pouring it through a sodium sulfate filtration funnel into a 250 mL flask.

6.4.2 Add some activated copper to the sample extract. If the gloss and color of the copper darkens, add additional copper to the extract until the copper does not change color.

6.4.3 Add boiling chips to the flask and concentrate the sample extract to about 1-2 mL on a water bath at 60°C.

6.4.4 Exchange the solvent of the extract to hexane by gradually adding small amount of hexane to the extract while the sample extract is being concentrated on the water bath. When the solvent in the extract is exchanged to hexane (no apparent boiling), purify the sample extract using the column chromatography procedures of the appropriate GERG SOP.

7.0 DOCUMENTATION REQUIREMENTS

Copies of the following applicable documents should accompany the sample set in a labeled manila folder:

Chain of Custody documents
Sample Information Sheet
Analysis Request Form
Laboratory Bench Sheet
Sample Dry Weight Sheets
Sample Action Request Form, if applicable
Other miscellaneous information

Appendix J

Texas A&M, Geochemical and Environmental Research Group
STANDARD OPERATING PROCECURES SOP-9017
Revision No. 6
March 5, 1993
QUANTITATIVE DETERMINATION OF CHLORINATED HYDROCARBONS

1.0 INTRODUCTION

The quantitative method described in this document determines chlorinated hydrocarbons (e.g. chlorinated pesticides and PCBs) in sample extracts. The method is based on high resolution, capillary gas chromatography using electron capture detection (GC/ECD).

Extracts should be prepared as described in the appropriate GERG SOPs.

Sample collection, preservation, storage and holding times are discussed under the analytical procedures for sample extraction and purification.

2.0 APPARATUS AND MATERIALS

A gas chromatograph with a split/splitless injection system, capillary column capability and an electron capture detector (ECD) is utilized.

2.1 GC Column

A 30-m long x 0.25-mm I.D. fused silica capillary column with DB-5 bonded phase (J&W Scientific or equivalent) should be used. The column should provide good resolution of chlorinated hydrocarbons, surrogates and internal standards.

2.2 Autosampler

The autosampler is capable of making 1-4 µL injections.

3.0 REAGENTS

3.1 Calibration Solution

The calibration solution is comprised of, at a minimum, the chlorinated hydrocarbons indicated with an asterisk in Table 1.

Table 1. Chlorinated Hydrocarbons of Interest.

Chlorinated Pesticides

Aldrin*	**Heptachlor Epoxide***	**o-p' DDT***
alpha-Chlordane*	**Hexachlorobenzene***	**p-p' DDT***
Dieldrin*	**Lindane***	**o-p' DDD***
Endrin*	**Mirex***	**p-p' DDD***
Heptachlor*	**Trans-Nonachlor***	**o-p' DDE***
		p-p' DDE*

Polychlorinated Biphenyls

Dichlorobiphenyls	**Pentachlorobiphenyls**	**Heptachlorobiphenyls**
7	**100**	**178**
8*	**88**	**187/182/159***
15	**92**	**183**
	84	**185**
Trichlorobiphenyls	**101***	**174**
18*	**99**	**177**
24	**83**	**171**
16/32	**97**	**172**
26	**87**	**180***
25	**85**	**191**
31	**110/77***	**170***
28*	**82**	**189**
33	**107/108**	
22	**118/108/149***	**Octachorobiphenyls**
37	**114**	**202**
	105*	**200**
Tetrachlorobiphenyls	**126***	**201**
45		**196**
46	**Hexachorobiphenyls**	**195***
52*	**136**	**194**
49	**151**	**205**
47/48	**144**	
44*	**149**	**Nonachlorobiphenyls**
42	**146**	**208**
41/64	**153***	**206***
40	**141**	
74	**137**	**Decachlorobiphenyls**
70	**138***	**209***
66*	**158**	
60/56	**129**	
77	**159**	
	128*	
	167	

[1]PCB number from: Ballschmiter, K. and M. Zell, 1980, Analysis of Polychlorinated Biphenyls (PCB) by Glass Capillary Gas Chromatography. Freesenius Z. Anal. Chem., 302: 20-31.

Calibration standards should be prepared in the concentration range of 5 to 200 ng/mL (at four concentrations) at a minimum. Internal standard and

surrogate compounds should be added at 100 ng/mL to all calibration standards.

3.2 Surrogate Spiking Solution

The surrogate compounds for all sample types are 4,4'-dibromooctofluorobiphenyl (DBOFB), PCB-103, and PCB-198. A surrogate solution is made by weighing an appropriate aliquot of pure material into a volumetric flask and diluting to volume with hexane. Surrogate standards are added to each sample at a concentration of ~10 times the MDL. For higher concentrations of chlorinated hydrocarbons, the surrogate standard concentrations are appropriately increased.

3.3 Internal Standard Solution

The internal standard for this analysis is tetrachloro-m-xylene (TCMX). An internal standard solution is made by weighing an appropriate aliquot of pure material into a volumetric flask and diluting to volume with hexane. Internal standard should be added to each sample extract to obtain a final concentration of approximately 100 ng/mL. For higher concentrations, the internal standard concentration is appropriately increased.

3.4 Matrix Recovery Spiking Solution

The matrix spiking solution consists of chlorinated pesticides and PCBs indicated with an asterisk in Table 1.

The matrix spike is added to samples at a concentration ~10x the MDL. If higher concentrations are expected the matrix spike is appropriately increased.

3.5 Retention Index Solution

The calibration mixture is also used as a retention index solution as well as aroclor mixtures.

4.0 PROCEDURE

4.1 Sample Extraction and Purification

Water samples are extracted and purified (optional) following GERG SOP-9014. Sediment samples are extracted and purified following GERG SOP-9015. Tissue samples are extracted and purified following GERG SOP-9016.

4.2 High Resolution GC-*ECD* Analysis

4.2.1 GC Conditions

For the analysis of chlorinated hydrocarbons, the analytical system, or its equivalent, should include at a minimum:

Instrument:	Hewlett-Packard 5880A or Varian 3500 Series
Features:	Split/splitless capillary inlet system, HP-1000 LAS 3357 data acquisition system
Inlet:	Splitless
Detector:	Electron Capture
Column:	0.25-mm I.D. x 30-m DB-5 fused silica capillary column (J&W Scientific)
Gases:	
Carrier:	Helium 1 mL/min
Make-Up:	Argon/methane (95/5) or Nitrogen, 20 ml/min.
Temperatures:	
Injection port:	275°C
Detector:	325°C
Oven Program:	100°C for 1 min., then 5°C/min. to 140°C, hold 1 min.; 1.5°C/min to 250°C, hold 1 min.; 10°C/min to 300°C, hold 5 min.

The GC oven temperature program may be modified to improve resolution.

Calibration:	Four-point calibration (5 or 20, 40, 80, and 200 ng/mL)
Quantification:	Surrogate standard/calibration

4.2.2 Calibration

Pesticide/PCB calibration is done as part of the analytical run. The four calibration mixtures are interspersed with actual samples during the GC/ECD analyses. The calibration curve is then based on these four standards. If the calibration curve has an r^2 of 0.995 or higher for all analytes present in the samples it is accepted, if not the calibration standards as well as all the samples must be reanalyzed by GC/ECD. This procedure is superior to the procedure where the instrument is initially calibrated at four points and then mid-level standards are run during the analytical run. This latter calibration only insures that mid-level samples remain in calibration. Since the ECD detector is nonlinear, a one-point check on its calibration is not as rigorous as calibration during the GC/ECD run.

4.2.3 Sample Analysis

As discussed in Section 4.2.2 calibration mixture, actual samples, and QA samples (blanks, matrix spikes, SRM, etc.) are run as one analytical sequence.

Sample injections of 1 to 4 µL are made with an autosampling device.

If the response for any peak exceeds the highest calibration solution, the extract is diluted, more surrogate solution added, and the sample reanalyzed for those analytes that exceed the calibration range.

4.2.4 Calculations

Concentrations in samples are based on surrogate standards added. All analyte concentrations are normally calculated from PCB-103 surrogate. The internal standard (TCMX) is used to calculate surrogate recoveries. In selected cases DBOFB and/or PCB-198 may be used to calculate selected analytes concentrations, if it can be demonstrated that they produce more reliable data (i.e., if matrix interference occurs with PCB-103) based on % recoveries in spiked blanks, matrix spikes, or reference materials.

5.0 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) REQUIREMENTS

5.1 Calibration Checks

A four-point calibration curve establishes the response of the detector. The calibration curve is prepared using a non-linear calibration equation of the form:

$$Y = A(x)^B$$

$$Y = (C_a/C_{su}) = A * (A_a/A_{su})^B$$

where:

A = Constant, slope of the line fit
B = Constant, polynomial coefficient for the line fit
C_a = Concentration of the analyte to be measured (ng/mL).
C_{su} = Concentration of the surrogate standard (ng/mL) (PCB 103).
A_a = Area for the analyte to be measured.
A_{su} = Area for the surrogate standard (PCB 103).

The calibration solutions that are analyzed as part of the analytical GC/ECD run, are preceded by no more than six samples and no more than six samples are run between calibration mixtures. Acceptance criteria for the calibration curve is outlined in Section 4.2.2.

5.2 Method Blank Analysis

An acceptable method blank analysis does not contain any target compound at concentration 3 times greater than the MDL. If the method blank does not meet these criteria, the analytical system is out of control and the source of the contamination must be investigated, corrective measures taken, and documented before further sample analysis proceeds.

5.3 Surrogate Standards Analysis

All samples and quality control samples are spiked with DBOFB, PCB 103 and PCB 198. The surrogate standard solution will be spiked into the sample prior to extraction in an attempt to minimize individual sample matrix effects associated with sample preparation and analysis.

The laboratory will take corrective action whenever the recovery of the surrogate used to quantitate is outside of 40 to 130 percent range.

The following corrective action will be taken when an out of control event occurs:

a. Calculations are checked to assure that no errors have been made.

b. The surrogate standard solutions are checked for degradation, contamination, etc., and instrument performance is checked.

c. If the surrogate could not be measured because the sample required dilution or only a portion of the sample was analyzed, or matrix interference occurs with only one surrogate, no corrective action is required. The surrogate recovery is properly annotated.

d. If the steps above fail to reveal a problem, the sample or extract is reanalyzed. If reanalysis of the extract yields surrogate recoveries within the stated limits, then the reanalysis data is reported. If upon reinjection, QA criteria are still violated, the sample will be submitted for re-extraction if sufficient sample is available. If the sample was completely consumed, the data will be reported but designated as outside the QA criteria.

5.4 Matrix Spike Analysis

Matrix spikes when required are analyzed with each sample set. A sample is randomly chosen, split into subsample(s) and subsample(s) are fortified with the matrix spike. The acceptable matrix spike recovery criteria are:

- The average recoveries for all compounds except HCB and Beta-BHC must fall between 40 and 120 percent. Recoveries of HCB and Beta-BHC are acceptable if they are greater than 10 percent.

If the matrix spike criteria are not met, the matrix spike will be reinjected on the GC. If the reinjected matrix spike analysis meets the criteria, then the reanalysis data is reported. If none of the analytes that are in violation are present in the sample, the violation is noted but no action is required. If analytes that are present in the sample are in violation, the entire batch of samples are submitted for re-extraction if sufficient sample is available. If the sample was completely consumed the data will be reported but designated as outside the QA criteria.

5.5 Method Detection Limit

The method detection limit is determined following the procedures outlined in Federal Register (1984), Vol. 49, No. 209: 198-199.

5.6 GC Resolution

The target compounds, surrogates and internal standard should be resolved from one another and from interfering compounds. When they are not, coelutions are documented.

5.7 Reference Material Analysis

When available, standard reference materials (SRM) or laboratory reference materials will be analyzed for chlorinated hydrocarbons. One sample will be analyzed per batch of samples. The result should agree within ±3 standard deviations of the mean of the previously reported data for laboratory reference material. For SRM the results should agree within 50 to 125% of certified values or ± 35% of reference values. The data produced are used to construct control charts.

6.0 CALCULATIONS

6.1 Chlorinated Hydrocarbon Calculations

All calculations are based on the surrogates added before extraction and purification. The actual sample concentration (C, see section 7.1 for reporting units) for each compound is calculated by the following formula:

$$C = A * (A_a/A_{su})^{B} * (I_{su}/S_{DW})$$

where:

A	=	Constant, slope of the curve fit
B	=	Constant, polynomial coefficient for the curve fit
A_a	=	Area for the analyte to be measured.
A_{su}	=	Area for the surrogate standard (PCB 103).
I_{su}	=	Amount of surrogate standard added to the sample.
S_{DW}	=	Sample dry weight.

6.2 Calculation Notes

6.2.1 To each sample, a specific amount of surrogate standard is added. The recovery of these compounds is monitored in each sample using the response of TCMX the internal standard (I_{gc}) added to the final extract just prior to GC/ECD analyses.

$$\text{Percent surrogate recovery} = (R_1)(R_2)(R_3)(R_4)(100)$$

where:

R_1 = Surrogate peak area/internal standard peak area in sample.
R_2 = Surrogate concentration/internal standard concentration in one of the calibration mixtures.
R_3 = ***Internal standard*** peak area/surrogate peak area in one of the calibration mixtures.
R_4 = Amount of internal standard (I_{gc}) added to sample just prior to GC analysis/amount of surrogate standard added to sample just prior to sample extraction.

7.0 REPORTING

7.1 Reporting Units

Data is reported in ng/g dry weight. If the data is required on a wet weight basis, the sample wet weight (S_{WW}) can be substituted in the equation in Section 6.1 for S_{DW}.

The effective minimum performance standard can be adjusted by decreasing final sample volume, increasing sample amount and/or increasing volume injected on the GC-ECD.

7.2 Minimum Method Performance Criteria

The minimum method performance standard for tissues is 0.5 ng/g for individual compounds.

7.3 Significant Figures

Results are reported to three (3) significant figures.

7.4 Surrogate Recovery

Surrogate recoveries are reported for each sample analyzed.

7.5 Matrix Spike

Matrix spike recoveries, when required, are reported for each batch of samples analyzed.

7.6 Reference Materials

When available the results of the analysis of reference materials is reported for each batch of samples analyzed.

Appendix K

Corrective Action Report
CAR #: _____

Report Initiation Date: _____ Area/Site: _____
Reported by: _____ Analyte/Activity: _____

State the nature of the problem, nonconformance or out-of-control situation:

_____
_____
_____

Affected sample #s / date(s) of sample collection: _____
Project: _____ Attached documentation (NA, COC): _____

Possible Causes and Corrective Actions Taken / Recommended:

_____
_____
_____

CAR routed to: _____ Date: _____

Supervisor: _____

Circle one: Tier 1 (does not affect final data integrity) Tier 2 (possibly affects final data integrity)

Corrective Actions (If actions are to be taken, include Responsible Party[1] and proposed completion date, where appropriate)

For specific incident: Taken To be taken _____
_____
_____

To prevent recurrences: Taken To be taken _____
_____
_____

Effect on data quality: _____

Responsible Supervisor: _____ Date: _____
Concurrence: _____

BUDG Project Manager: _____ Date: _____

CRASR QAO: _____ Date: _____

1. Party responsible for implementing corrective action is also responsible for notifying QAO of completion and outcome of corrective action.

This page intentionally left blank.

Appendix L

Data Review Checklist

Field Data Review

Y, N, or N/A

A. Field documentation includes the following:
   (1) Identification of individual collecting samples(s)? _____
   (2) Sample ID number and site location? _____
   (3) Sample collection date and time? _____
   (4) Site observations (i.e. weather, etc.)? _____
   (5) Unusual occurrences that may affect sample? _____
   (6) Sample collection problems? _____
B. Chain of custody record properly filled out and available for review? _____

Data Format and Structure

A. Are there any duplicate sample ID numbers? _____
B. Are station location numbers assigned? _____
C. Are sampling dates in the correct format, DD/MM/YY? _____
D. Are samples listed in the correct units? _____
E. Is the sampling time entered? _____

Data Quality Review

A. Appropriate holding times confirmed? _____
B. MDLs consistent with those in the QAPP? _____
C. Outliers confirmed and documented? _____
D. Documentation (verified error log) provided to TSSWCB? _____
E. Checks on correctness of analysis or data reasonableness performed? (i.e. - Is ortho-phosphorus greater that total phosphorus?) _____
F. Have at least 10% of the data in the database been reviewed against the data sheets? _____

Explain any answers that may indicate a problem with the data (attach another page if necessary): _____

Data Range: _____

Data Source: _____

Field Supervisor Signature: _____ Date: _____

Data Supervisor Signature: _____ Date: _____

Project Leader Signature: _____ Date: _____

Appendix M

Core Sub-sampling Form

Reservoir: _____ Core: _____

Sampler: _____ Date: _____

Sample No.	Depth Interval	Container Wt.	Wet Wt.	Dry Wt.	Bulk Wt.	Penetration Resistance	Physical Appearance

This page intentionally left blank.

Appendix N

Chain-of-Custody Record

Sampler(s): _____ Page: _____ of _____

Sample Location (s): _____

Station ID	Collection Date	Time of Collection	Station Location/Description	Type of Collection	Number/Type of Containers

Date: _____ Time: _____

Relinquished by: _____

Received by: _____

Date: _____ Time: _____

Relinquished by: _____

Received by: _____

This page intentionally left blank.

Appendix O

CRASR Laboratory Sample Analysis Form

Sample ID	Sample Type	Replicate Number	Repeat Number	Cup Number	Manual Dilution Factor	Auto Dilution Factor	Weight (Units)	Weight	Weight Units

Detection Date	Detection Time	User Name	Run File Name	Description	Channel Number	Analyte Name	Peak Concentration	Concentration Units

Peak Area	Peak Height	Calibration Equation	Retention Time	Inject to Peak Start