QUALITY ASSURANCE PROJECT PLAN

for

The Upper Neuse River Basin Association
Water Quality Monitoring Program

Prepared for:
The Upper Neuse River Basin Association
P.O. Box 270
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Program Administered and Plan Prepared by:
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Approved by the
North Carolina
Department of Environment and Natural Resources
Division of Water Resources

July 30, 2014

Version 1.0

ABBREVIATIONS

BOD_5: biochemical oxygen demand, 5-day
c.u.: color units
CAAE: Center for Applied Aquatic Ecology, NCSU
CASTNET: Clean Air Status and Trends Network
$CBOD_5$: carbonaceous biochemical oxygen demand, 5-day
Chl *a*: chlorophyll *a*
DO: dissolved oxygen
DOC: dissolved organic carbon
DWR: Division of Water Resources, NC-DENR
EFDC: environmental fluid dynamics code
EPA: U.S. Environmental Protection Agency
ISB: Intensive Survey Branch, NC-DENR
LCS: laboratory control sample
MDL: method detection limit
NADP: National Atmospheric Deposition Program
NC: North Carolina
NCAC: North Carolina Administrative Code
NC-DENR: North Carolina Department of Environment and Natural Resources
NCSU: North Carolina State University
NH_3: ammonia
$NO_2 + NO_3$: nitrite plus nitrate
NOAA NCDC: National Oceanic and Atmospheric Administration National Climatic Data Center
NTU: nephelometric turbidity units
PO_4: phosphate
PQL: practical quantitation limit
Pt-Co: platinum-cobalt
QA: quality assurance
QAM: Quality Assurance Manual
QAPP: Quality Assurance Project Plan
QC: quality control
RPD: relative percent difference
SLPH: State Laboratory of Public Health, NC Department of Health and Human Services
SM: Standard Methods for the Examination of Water and Wastewater
SOP: standard operating procedure
SRP: soluble reactive phosphorus (sample filtered, but not digested)
SUVA: specific ultraviolet absorbance
TKN: total Kjeldahl nitrogen
TOC: total organic carbon
TP: total phosphorus (sample digested, but not filtered)
TRP: total reactive phosphorus (sample not digested and not filtered)
TSP: total soluble phosphorus (sample filtered and digested)
TSS: total suspended solids
UNRBA: Upper Neuse River Basin Association
USGS: United States Geological Survey
UV: ultraviolet

REVISION LOG

UNRBA Monitoring Program
Quality Assurance Project Plan

Date	Version Edited	Section	Changes/Updates	Editor
30 July 2014	1.0	All	Initial Approved QAPP	N/A

SECTION A — **PROJECT MANAGEMENT**

A.1 Signature and Approval Sheet

Upper Neuse River Basin Association, Water Quality Monitoring Program
Quality Assurance Project Plan, Version 1.0

Approved by:

Lauren Elmore, Cardno
Project Manager — Date: 7/31/2014

Matthew Van de Bogert, Cardno
Project Coordinator and Quality Assurance Manager — Date: July 30, 2014

Doug Durbin, Cardno
Principal in Charge — Date: 8-14-14

Mark Oliveira, Environment 1, Inc.
President & Quality Assurance Manager — Date: 8/22/14

Forrest Westall, UNRBA
Executive Director — Date: 8/20/2014

Pam Hemminger, UNRBA
Chair, Board of Directors — Date: August 20, 2014

Tom Fransen, NC Division of Water Resources
Water Planning Section Chief — Date: 8/22/14

Dianne Reid, NC Division of Water Resources
Water Sciences Section Chief — Date: 9/8/2014

A.2 Table of Contents

A.3 Distribution List

Primary Distribution:

Upper Neuse River Basin Association
Forrest Westall, Executive Director
Haywood Phthisic, Assistant to Executive Director

NC Department of Environment and Natural Resources, Division of Water Resources
Dianne Reid, Water Sciences Section Chief
Tom Fransen, Water Planning Section Chief
Kathy Stecker, Modeling and Assessment Branch Chief
Steve Kroeger, Ecosystems Branch Chief
John Huisman, Environmental Consultant
Cam McNutt, Water Planning Section, Modeling and Assessment Branch

Cardno
Lauren Elmore, Project Manager
Matthew Van de Bogert, Project Coordinator and QA Manager
Doug Durbin, Principal in Charge
Chris Mickle, Database Administrator

Environment 1, Inc.
Mark Oliveira, President, Project QA/QC Manager, Field Supervisor
Steve Jones, Laboratory Supervisor
Chad Davis, Field Staff
Ashley Vanderburg, Field Staff

A.4 Project Organization

Introduction

The UNRBA Water Quality Monitoring Program is conducted under the direction of the Upper Neuse River Basin Association (UNRBA). The UNRBA water quality monitoring program is aimed at fulfilling the association's mission to collect and analyze data for the development and evaluation of strategies to reduce, control, and manage pollutant discharge (Box A.4.1). The purpose of this QAPP is to provide users of any data collected as part of this program with documentation that clearly describes the quality systems used to obtain the data. This QAPP will assist data users to avoid any conflicts in data use that do not meet the demands of their specific data quality objectives.

Box A.4.1. The mission of the UNRBA.

The mission of the UNRBA is to preserve the water quality of the Upper Neuse River Basin through innovative and cost-effective pollution reduction strategies, and to constitute a forum to cooperate on water supply issues within the Upper Neuse River Basin by:

- *Forming a coalition of units of local government, public and private agencies, and other interested and affected communities, organizations, businesses and individuals to secure and pool financial resources and expertise;*
- *Collecting and analyzing information and data and developing, evaluating and implementing strategies to reduce, control and manage pollutant discharge; and*
- *Providing accurate technical, management, regulatory and legal recommendations regarding the implementation of strategies and appropriate effluent limitations on discharges into the Upper Neuse River Basin.*

The day-to-day operations of data collection and quality assurance procedures which occur under the guidance of this QAPP will be directed by Cardno. The Monitoring Program will be overseen by the UNRBA. The UNRBA Executive Director, Forrest Westall, serves as the primary point of contact with Cardno and its subcontractors (hereafter referred to as the Cardno Project Team). The UNRBA Executive Director along with the UNRBA Path Forward Committee will provide general project guidance.

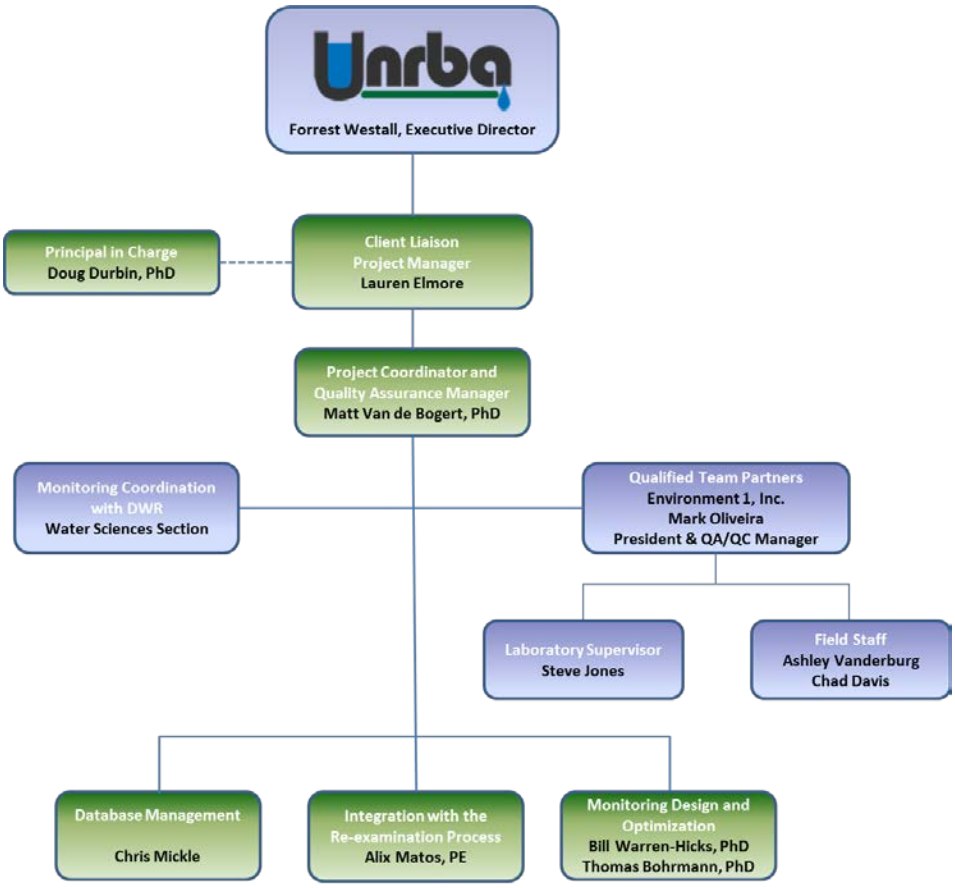

Figure A.4.1. UNRBA Monitoring Program Organizational Chart

Project Management and Oversight

Project Manager

Lauren Elmore, Cardno

- Responsible for ensuring that the monitoring program is conducted in accordance with all relevant QAPPs and standard operating procedures (SOPs)
- Reviews and approves all reports, work plans, corrective actions, QAPP, and any other major work products and their revisions
- In consultation with UNRBA Executive Director, approves changes to program and ensures changes comply with UNRBA goals and North Carolina Department of Environment and Natural Resources Division of Water Resources (henceforth, DWR) requirements
- Reports to UNRBA Executive Director and keeps Executive Director apprised of monitoring program status and progress

Project Coordinator and Quality Assurance Manager

Matthew Van de Bogert, Cardno

- Acts as liaison between program management, field staff, and analytical laboratory
- Coordinates logistics of program, such as maintaining sampling schedule, producing and distributing sample submission forms to field staff, and maintaining station information database
- Responds to issues raised by any program participant or outside party, identifies root causes and recommends response actions to the Project Manager
- Communicates needed or suggested changes to the Project Manager for approval
- Performs data management tasks including tracking samples and results, reviewing data, identifying and correcting errors, uploading data to final database upon verification of adherence to all aspects of this QAPP
- Performs field and lab audits to assure compliance with this QAPP and associated SOPs and communicates needed corrective actions to Project Manager and field staff supervisors when needed
- Documents QA practices of the UNRBA monitoring program
- Maintains the UNRBA monitoring QAPP
- Develops and recommends QA/QC improvements

Database and Web Interface Administrator

Chris Mickle, Cardno

- Designs and maintains database structure, web interface, data archives and backups
- Works with Project Manager and Project Coordinator to respond to issues raised by program participants with respect to database, data entry, and online data access

Data Generation (Measurements and Analyses)

QA/QC Manager, Field Supervisor

Mark Oliveira, President, Environment 1, Inc.

- Primary contact between Cardno and Environment 1, Inc.
- Schedules monitoring program according to QAPP guidelines
- Responsible for QAPP compliance
- Notifies Project Manager of any issues encountered
- Responsible for enforcing response or corrective actions of supervised field staff as necessary.
- Responsible for all data submissions/uploads
- Reviews field calibration sheets and results of all quality control checks after each monitoring event to assess the adequacy of the control checks and to identify any problems
- Notifies Project QA Manager in writing of any quality control check issues
- Proposes corrective actions for QA/QC issues.
- Serves as the point of contact for questions relating to quality control of reported data

Laboratory Supervisor

Steve Jones, Environment 1, Inc.

- Manages laboratory which performs all analyses on samples taken as part of the UNRBA monitoring program
- Responsible for oversight of all analytical activities and for ensuring that all analyses are performed in accordance with the standard operating procedures for this project
- Maintains laboratory certification from DWR for all analyses performed for the UNRBA

Field Staff

Ashley Vanderburg and Chad Davis, Environment 1, Inc.

- Performs all field activities including field measurements, observations, and sampling in accordance with QAPP and SOPs
- Notifies Environment 1, Inc. Field Supervisor or Cardno Project Manager of any issues encountered

Primary data end-users

UNRBA

Forrest Westall, Executive Director

- Liaison between the UNRBA (primary data end-user) and Cardno staff
- Receives semi-annual reports from Cardno on monitoring program
- Facilitates interactions between UNRBA Board of Directors, the Path Forward Committee, and Cardno for annual review of and updates to the monitoring program prior to the start of each fiscal year
- Provides input to the Project Manager on changes needed to the monitoring program as part of a continuous program assessment process

NC DENR

Division of Water Resources (DWR)

- Reviews, provides comments, and approves QAPP and subsequent revisions.

A.5 Problem Definition and Background

The Upper Neuse River Basin Association (UNRBA) has contracted with Cardno to develop and administer a monitoring program to collect data necessary to assess water quality in Falls Lake and its watershed. This data will be used to support a re-examination of Stage II of the Falls Lake Nutrient Management Strategy (NCAC 15A 02B.0275(5)). This Quality Assurance Project Plan (QAPP) is intended to cover data collected under the administration of the UNRBA by Cardno and does not supplant any existing QAPPs of member organizations. The procedures outlined in this QAPP are intended to follow those in existing Division of Water Resources (DWR) QAPPs as closely as possible

so that the data collected under this monitoring program meet the same Quality Assurance/Quality Control standards as data collected by DWR.

To meet requirements outlined in the Falls Lake Rules, DWR must review and approve any monitoring study plan to assure that data collected under this program are acceptable for potential regulatory use. One objective of this QAPP, in conjunction with the standard operating procedures (SOPs) in the Appendices, is to provide the documentation necessary to demonstrate compliance with DWR Quality Assurance standards.

Specific goals of the monitoring program include

- facilitating estimates of nutrient, carbon, sediment, and chlorophyll loading to Falls Lake
- aiding in parameterization of water quality models, and
- providing water quality data at jurisdictional boundaries within the Falls Lake watershed.

The monitoring plan is designed to be an adaptive program. The results of early monitoring activities and initial analyses may be used to refine the monitoring program on an annual or semi-annual basis. Most monitoring changes are expected to relate to the specific locations being sampled or the frequency with which samples are taken. These changes will not result in revisions of this QAPP. If parameters not included in this QAPP are proposed for later inclusion in the routine monitoring program to support efforts requiring DWR approval per the Falls Lake Rules, they will be documented in revised versions of this QAPP, cataloged in the Revision Log at the beginning of the document, and provided to DWR for review.

To facilitate UNRBA's data management needs, Cardno will create and maintain a database that includes data generated under sections B.1 through B.8 of this QAPP as well as data collected by federal, state, and/or local agencies as described in section B.9. All database entries will be tracked according to the data-generating organization. Data included in the database will be limited to data collected within Falls Lake and at sites defined as lake loading sites or jurisdictional boundary sites in the Monitoring Plan (Appendix A). It will also include any special studies conducted under the Monitoring Plan. The database will not include data collected by UNRBA member jurisdictions at sites other than those specified in the Monitoring Plan.

Data produced by the UNRBA monitoring program will be provided to the UNRBA members to support the goals and efforts of that organization. UNRBA anticipates using this data to facilitate updates to the Falls Lake Nutrient Response model built using the Environmental Fluid Dynamics Code (EFDC). The model structure and equations are described in the Falls Lake Nutrient Response Model Final Report (NC-DENR 2009). Data will be used to refine loading estimates as well as concentrations of key water quality parameters within Falls Lake. Data collected will also be used to refine the sampling program. Sampling locations or sampling frequencies which produce redundant or uninformative data with respect to the modeling framework may be discontinued, suspended, or reduced, while additional locations may be added or sampling frequencies increased.

Data collected under this program will also be provided to DWR annually.

A.6 Project Description and Schedule

Overview

The overall goal of the field sampling program is to provide an accurate and representative picture of the current water quality conditions at specific sampling stations throughout the watershed. The environmental data collected under this task may be used as input to or calibration data for water quality and hydrologic models developed or refined under subsequent UNRBA tasks. The UNRBA monitoring program will take place over four years with the possibility of one additional year if needed and approved by the UNRBA. Routine monitoring under this program may consist of efforts categorized into three different categories each with its own set of locations, schedule, and parameters to be monitored.

A. Routine monitoring of tributaries near the point where they enter Falls Lake to improve estimates of nutrient, carbon, chlorophyll, and sediment loading from the tributaries.
B. Routine monitoring of water quality at jurisdictional boundaries to provide information on water quality at multiple locations for individual jurisdictions.
C. Routine monitoring of water quality at locations within Falls Lake itself. (Initially there are no current UNRBA monitoring locations within Falls Lake itself but modifications may be considered by the UNRBA in the future.)

A. Lake loading locations

Locations monitored for quantifying lake loading include one station on each of the 17 Falls Lake tributaries which are modeled as part of the Falls Lake Nutrient Response Model. In addition, the Little River will be monitored before its confluence with the Eno River. A current map and table of sites, coordinates, and sampling frequencies can be found in Appendix 1. Parameters which will initially be monitored at the lake loading sites can be found in Appendix 1, but parameters may be added or removed based on data analysis or tributary-specific concerns. Table A.6.1 lists the parameters which may be measured under this QAPP, though not all of these will be measured at every location. The project manager will maintain a current list and historical record of monitoring stations, parameters measured, and sampling frequency. Any new parameters added to the routine monitoring program which are not included in the most current version of the QAPP will be addressed in a revised QAPP which will be re-submitted for DWR review. The frequency of sampling at lake loading sites may vary from site-to-site. The UNRBA will determine and review sampling frequency annually prior to the start of each fiscal year with input from reports and recommendations from Cardno.

Table A.6.1. Water quality parameters which may be measured as part of this monitoring program.

Field Measurements	Laboratory Analyses
Water temperature	Total Kjeldahl nitrogen
Specific conductance	Soluble[1] Kjeldahl nitrogen
Dissolved Oxygen	Nitrate + nitrite
pH	Ammonia
Air temperature	Total phosphorus (TP)
Turbidity	Total soluble[1] phosphorus (TSP)
Instantaneous discharge	Total reactive P (TRP[2]) ("total orthophosphate")
	Soluble reactive P (SRP[1,2]) ("soluble orthophosphate")
	Total organic carbon
	Dissolved organic carbon
	Chlorophyll *a*
	Total suspended solids
	Turbidity
	Color (Pt-Co color units and absorbance at 440nm)
	Tannins and Lignin
	UV absorbance (at 254nm) (for SUVA calculation)
	Carbonaceous biochemical oxygen demand ($CBOD_5$)
	Biochemical oxygen demand (BOD_5)

[1] For the purposes of this QAPP, the term "soluble" is interchangeable with "dissolved" or "filterable".

[2] Reactive phosphorus is often called orthophosphate, however the method used for measuring this quantity is not 100% specific to orthophosphate and thus "reactive phosphorus" is the preferred term because it specifies the inclusion of all forms of phosphorus which react to the reagents used in this method.

B. Jurisdictional boundary locations

Jurisdictional boundary sites include tributary locations at municipal and county boundaries which have been identified by the UNRBA for routine monitoring. The specific locations monitored, the frequency of monitoring, and the specific parameters to be measured may vary in time; the monitoring plan will be reviewed annually by the UNRBA. A map and table of locations, coordinates, and sampling frequencies for the initial set of jurisdictional boundary sites are included in Appendix 1. The project manager will maintain a current list and historical record of monitoring stations, parameters measured, and sampling frequency.

Initial parameters to be measured at jurisdictional boundary sites are a subset of those listed in Table A.6.1. Any new parameters added to the routine monitoring program which are not included in the most current version of the QAPP will be addressed in a revised QAPP which will be re-submitted for review.

C. In-lake monitoring

UNRBA may choose to temporally or spatially supplement the monitoring already conducted by DWR, the City of Raleigh, the City of Durham, or the Center for Applied Aquatic Ecology in Falls Lake or to add sampling for parameters not collected by those organizations now or in the future. Initially, there are no in-lake sites included for routine sampling in the monitoring plan, however, this QAPP will cover sampling and analytical methods and quality assurance/quality control protocols for lake sampling for

the parameters listed in Table A.6.1, except instantaneous discharge which is not applicable to lentic locations.

Measurement Methods Overview

Field Measurements

Measurements made in the field are temporally discrete and made *in situ* whenever possible by field staff at the time of the station visit. If *in situ* measurements cannot be made (e.g. probe cords may be too short to cover the distance between a bridge sampling location and the water body), parameters may be measured from a sample as long as the SOPs specified for each parameter are followed and measurements are made immediately after the sample is taken. All field measurements are performed in accordance with Environment 1, Inc. SOP's (Appendix 6), DWR Wastewater/Groundwater Laboratory Certification Approved Procedures for Field Analysis (Revised April 2013) (Appendix 2) and/or the DWR Intensive Survey Branch (ISB) SOP version 2.1 (Revised December 2013) (Appendix 3), as appropriate. Turbidity may be measured in the field using equipment which meets the specifications of EPA Method 180.1 Revision 2.

Specific field measurements and sampling methods are documented in section *B.2: Sampling Methods*.

Analytical Samples

Lab analyses will be conducted by Environment 1, Inc., a DWR certified laboratory with experience working with samples collected under ambient conditions and the State's Monitoring Coalition Program. The laboratory's analytical methodologies are not managed under this QAPP, except to specify that this laboratory has, and must maintain, certification from the DWR Laboratory Certification Program or the State Laboratory of Public Health for the parameters currently certified by these agencies and as specified in Table B.1.3. The laboratory will meet the criteria for reporting levels, analytical methods, accuracy, and precision which are specified in this QAPP and are appropriate for ambient monitoring conditions.

The specific analytical methods to be used are listed in section *B.4: Analytical Methods* of this document. Precision and accuracy targets are described in section *A.7: Quality Objectives and Criteria*.

Data Management

To facilitate the organized collection of data along with systematic review for quality assurance, the UNRBA will use a web-based environmental data and document management systems. The data management system will facilitate the upload, review and validation of monitoring data prior to inclusion in the project database. The document management system will be used to archive field data sheets, calibration sheets, photographs, laboratory and quality control reports for each monitoring event. Data will be uploaded by field and laboratory staff into a "holding area" of the data management system prior to review and validation of the data into the official database. Field and laboratory staff will be responsible for reviewing data submittals prior to uploading to the data management system for typographical errors and omissions. The Quality Assurance Manager will validate all uploads per the quality assurance protocols of this QAPP prior to appending data to the project database. Details of the quality assurance procedures associated with data management can be found in section B.10: Data Management.

A.7 Quality Objectives and Criteria

The data collected in support of the UNRBAs monitoring program will meet the quality objectives detailed in this section.

Accuracy

Accuracy is a measure of agreement between an observed value and an accepted reference or true value. The measurement of accuracy may include components of random error or systematic error and bias. Laboratory accuracy can be assessed through laboratory control samples (LCS, analysis of a known value), method blanks (MB, analysis of sample with no analyte present), and matrix spike samples (MS, analysis of a known quantity of analyte added to a field sample). Biases due to field procedures will be assessed via equipment blanks and field filter blanks.

Field Accuracy Objectives

Field accuracy is assessed through equipment blanks and field filter blanks (for analyses requiring immediate filtration in the field). Equipment blanks will be collected at a rate of 1 per 20 samples when an intermediary device is used to collect samples (e.g. pole sampler, lab line, van Dorn bottle, or similar devices).

Sampling equipment may become contaminated through the normal course of monitoring. If the equipment is not properly cleaned and rinsed, subsequent samples may become contaminated from residue left from previous locations. Equipment blanks will be used to assess cross-contamination of samples by equipment or sampling techniques. Equipment blanks are obtained by running reagent grade deionized water through the sampling equipment which is then submitted to the analytical laboratory for analysis. Blank samples should be collected from a final deionized water rinse of the specified equipment after the equipment has been cleaned in accordance with appropriate cleaning procedures per standard operating procedures (Appendix 3). Blanks must be treated in the same manner as field samples, including handling, preservation, and hold times.

Additionally, equipment blanks for filtration equipment used for collecting samples of soluble nutrients (Total soluble phosphorus (TSP), soluble reactive phosphorus (SRP), and soluble TKN) will be collected at the start and end of each sampling day when field filtration occurs. Field filtration blanks are obtained by filtering reagent grade deionized water through filtration equipment (including filter) and pouring into separate containers for laboratory analyses. Field filtration blanks should be collected after the filtering apparatus has been cleaned with deionized water according to the appropriate cleaning procedures. Sample preservation, handling, and hold times must be consistent for blanks and field samples.

Equipment blanks should have reported values less than ½ of the reporting limit. Equipment blanks with values higher than ½ of the reporting limit must be reported to the project manager for resolution. A summary of QC objectives for field methods with frequency, acceptance criteria, and necessary corrective actions is provided in Table A.7.1.

Table A.7.1. Quality Control Objectives for Field Methods.

QC Sample	Data Quality Indicator	Frequency	Acceptance Criteria	Corrective Action
Equipment Blank	Accuracy/ Bias as contamination	1/20 field samples	Concentration < ½ RL	Contact Project Manager
Field Blank - Filtration Equipment	Accuracy/ Bias as contamination	2/5 field samples	Concentration < ½ RL	Contact Project Manger
Field Duplicate	Precision	1/10 field samples	Parameter-specific. See Table A.7.3	Qualify associated field data and/or resample

Laboratory Accuracy Objectives

Laboratory accuracy will be assessed through the analysis of method blanks, laboratory control samples (LCS), and matrix spike samples (MS). Blanks should have concentrations less than ½ of the reporting level. The percent recovery (%R) for LCS and MS samples should meet the objectives identified in the appropriate columns of Table A.7.2. Laboratory Control Samples (LCS) will be analyzed at the rate of 1 LCS per batch of up to 20 samples. In the event that the %R of a LCS falls outside of the range specified in Table A.7.2., all associated samples should be re-prepared and reanalyzed. Matrix Spike (MS) samples will be analyzed for those parameters whose methods require it at the rate of 1 per batch of up to 20 samples. If the %R for MS samples falls outside of the range specified in Table A.7.2., all associated samples should be re-prepared and reanalyzed. If the problem recurs, it should be justified in the data report and data values will be qualified in the database with the qualifier code J2.

Precision

Precision is a measure of the degree of reproducibility of repetitive measurements under a given set of analytical conditions (exclusive of field sampling variability). It is the degree of mutual agreement among independent measurements as the result of repeated application of the same process under similar conditions. Precision is documented on the basis of replicate analysis, including field replicates, laboratory duplicate samples, or matrix spike duplicate samples. Precision may also be assessed by comparing results of split samples analyzed by independent laboratories as described in section B.5.

Parameter-specific precision objectives for field and laboratory measurements are provided in Table A.7.3. Matrix spike/matrix spike duplicate (MS/MSD) samples will be used where indicated in Table A.7.3 to evaluate analytical precision and will be used as a basis for qualifying data where necessary. Lab duplicates will be used to document precision at ambient concentrations, but RPD values for lab duplicates which are outside the specified criteria will not necessarily lead to qualified or discarded data if LCS and MS/MSD samples otherwise show the method and batch to be in control. Following the suggested guidelines of Mitchell (2006), the criteria for precision will only be applied to samples with measured concentrations which are at least five times greater than the method detection limit. Duplicate samples which have low concentrations of analyte may have a higher RPD because the same absolute value of analytical error applied to a lower sample concentration will be associated with a larger percent error.

Field Precision Objectives

Field precision for samples analyzed in the laboratory is assessed through duplicate sample analyses. Field duplicate samples will be collected at a frequency of approximately 10% as detailed in section B.5.

Duplicates are produced by splitting a single sample into two or more aliquots immediately after the sample is collected. Each aliquot is placed into a separate container and analyzed separately. Field duplicate samples will not be collected for soluble nutrients (e.g. total soluble phosphorus, soluble reactive phosphorus (SRP, or dissolved orthophosphate), or soluble TKN). Precision for these parameters will be determined from the associated total (non-filtered) nutrient analysis. Field filter blanks will be used to assess bias from contamination from filters or the filter apparatus for these parameters.

The metric used for precision is the relative percent difference (RPD) between the results of the duplicate samples calculated as

$$RPD = \frac{|C_A - C_B|}{0.5(C_A + C_B)} \times 100$$

where C_A = measured concentration of duplicate sample A
C_B = measured concentration of duplicate sample B

When the precision of field duplicates exceeds the acceptance criteria listed in table A.7.3, the associated data will be evaluated by the Laboratory QA/QC Manager and the Project QA Manager and will be qualified if appropriate. If the exceedance is due to low concentrations of analyte (e.g. if absolute error is not large and the RPD is within the laboratory's calculated concentration-specific range for analytical precision given in Table A.7.3) and the method is otherwise in control, the data will not be qualified. The project manager will be notified when field duplicates exceed the precision acceptance criteria to assess the issue and to determine if changes to field procedures are necessary.

The precision of physical parameter readings (e.g. dissolved oxygen, pH, and conductivity) is assessed by comparing the instrument calibration readings with the post-check readings. Meters will be calibrated at the beginning of each field day and calibrations will be checked after approximately four hours and again after the last sample of the day. Specific conductance must read +/- 10% of the true value of the standard used. The pH readings must be +/- 0.2 s.u. of the check buffers. The dissolved oxygen reading must be +/- 0.5 mg/l of the saturation value. If the calibration check criteria are exceeded, the instrument will be recalibrated and the associated field data will be qualified, resampled, or deleted.

Laboratory Precision Objectives

The precision of laboratory analyses are assessed by comparing laboratory replicate analyses or by comparing matrix spikes (MS) with matrix spike duplicates (MSD) as prescribed by the specified analytical method for each parameter. Laboratory duplicates or matrix spike duplicates are conducted at a frequency of 1 per batch of up to 20 samples. If the relative percent difference (RPD) exceeds the acceptable criteria for any parameter (Table A.7.3), results will be reviewed with the lab supervisor. Samples in the affected batch will be reanalyzed or results will be justified in the data report. Generally, no corrective action is taken for matrix spike results exceeding the control limits as long as the LCS recoveries are acceptable.

Ideally, samples split between laboratories ("split samples") would meet the same precision criteria as field duplicates (Table A.7.3). However, split samples analyzed by separate laboratories using different equipment with different noise levels cannot be expected to meet the same rigor as duplicate samples analyzed by a single laboratory using one piece of equipment. Furthermore, analyte concentrations in split samples may be near the reporting limit and achieving these precision targets (expressed as percent difference) on very low concentrations may not be possible. Therefore, split sample precision values outside of this range will not automatically result in qualification of data, but will be reviewed by the Project Manager in consultation with the Laboratory QA/QC manager. An action plan will be developed only if necessary based on professional judgment and discussion with DWR. The results of all split sampling efforts and any associated action plans will be documented in the reports to UNRBA described in section A.9. These reports will also provide written documentation of any data which are rejected as a result of the split sampling effort along with the reasons for these rejections.

Required Practical Quantitation Limits

The practical quantitation limits (PQLs) required for the UNRBA's monitoring objectives are reported in table A.7.2. In addition to meeting the PQLs specified, Environment 1 will maintain up-to-date method detection limits (MDLs) for the analytical methods used in the project. These MDLs must support the specified reporting limits and will be recorded in the project database. MDLs may be updated by results of new studies using the method specified in the Federal Register, 40 CFR Part 136 Appendix B. Specifically, MDLs will be calculated as the product of the standard deviation of at least 7 replicate analyses times the student's t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

Measured values which are above the laboratory's method detection limit but below the specified reporting level will be reported as measured but qualified with the data qualifier code N3. These data may be used to indicate if improvements in reporting levels would significantly reduce the frequency of censored values in the data set. Measured values below the method detection limit will be reported as the reporting limit along with the qualifier code U.

Table A.7.2. Accuracy objectives for laboratory analyses and required reporting limits for the UNRBA monitoring program.

Parameter	Data Accuracy Objectives (% recovery)		Required Reporting Limits	
	LCS[1]	Matrix Spike	Analysis Method(s)	PQL[2]
Total suspended solids, TSS (LCS analyzed quarterly)	mfg.[3]	NA	SM 2540 D - 1997	2.5 mg/L
Turbidity	90-110%	NA	SM 2130 B - 2001 EPA 180.1 Rev 2.0	1 NTU
Chlorophyll *a*	NA[4]	NA	EPA 445.0 Rev 1.2	1 µg/L
5-day carbonaceous biochemical oxygen demand, CBOD5	80-120%	NA	SM 5210 B - 2001	2.0 mg/L
UV absorbance at 254nm	85-115%	NA	EPA 415.3 Rev 1.2 SM 5910 B-2001[5]	0.001 cm^{-1}
Color, (Pt-Co units)	NA	NA	SM 2120 B[6]	5 c.u.
Visible Absorbance at 440nm	90-110%[7]	NA	Cuthbert and del Giorgio (1992)[8]	0.001 cm^{-1}
Total organic carbon, TOC	90-110%	75-125%	SM 5310 C - 2000	1 mg/L
Dissolved organic carbon, DOC	90-110%	75-125%	SM 5310 C - 2000	1 mg/L
Tannins and Lignin	mfg	80-120%	SM 5550	0.2 mg/L
Total phosphorus, TP	85-115%	80-120%	EPA 365.4 (1974)	0.02 mg/L
Total soluble phosphorus , TSP	85-115%	80-120%	EPA 365.4 (1974)	0.02 mg/L
Total reactive phosphorus, TRP ("total orthophosphate")	85-115%	80-120%	SM 4500 P E - 1999	0.01 mg/L
Soluble reactive phosphorus, SRP ("dissolved orthophosphate")	85-115%	80-120%	SM 4500 P E - 1999	0.01 mg/L
Ammonia, total, NH_3	85-115%	80-120%	EPA 350.1 Rev. 2.0 (1993)	0.01 mg/L
Nitrite + Nitrate, $NO_2 + NO_3$,	85-115%	80-120%	EPA 353.2 Rev 2.0 (1993)	0.01 mg/L
Total Kjeldahl Nitrogen, TKN	85-115%	80-120%	EPA 351.2, Rev 2.0 (1993)	0.2 mg/L
Soluble Kjeldahl Nitrogen	85-115%	80-120%	EPA 351.2, Rev 2.0 (1993)	0.2 mg/L

[1] LCS: laboratory control sample
[2] PQL: practical quantitation limit
[3] mfg: outside quality control standards are purchased and the manufacturer's published limits are used.
[4] Accuracy of chlorophyll *a* analyses will be assessed through annual participation in DWR's Chlorophyll *a* round robin.
[5] Certification through NC SLPH
[6] Per section 8.3.6 of the DWR Laboratory section's QAM (2003), EPA Region 4 has approved the use of a spectrophotometer operating at a single wavelength (460nm) in place of visual comparison for this analysis.
[7] Under evaluation
[8] Cuthbert, I.D. and P. del Giorgio. 1992. Toward a standard method of measuring color in freshwater. Limnology and Oceanography. 37: 1319-1326.

Table A.7.3. Precision objectives and criteria

Parameter	Field Precision – RPD		Analytical Precision - RPD		Empirical Precision achieved by Environment 1[1]
	Estimated By	Objective	Estimated By	Objective	
Total suspended solids, TSS	Field duplicates	≤ 30%	Lab duplicate	≤ 30%	≤ 10%
Turbidity	Field duplicates	≤ 40%	Lab duplicate	≤ 30%	≤ 10%
Chlorophyll *a*	Field duplicates	≤ 30%	Lab duplicate	≤ 20%	≤ 10%
5-day carbonaceous biochemical oxygen demand, CBOD5	Field duplicates	≤ 40%	Lab duplicate	≤ 30%	≤ 30%
UV absorbance at 254nm	Field duplicates	≤ 30%	Lab duplicate	≤ 20%	≤ 20%
Color, (Pt-Co units)	Field duplicates	≤ 10 units	Lab duplicate	≤ 5 units	≤ 5 units
Color, Absorbance at 440nm	Field duplicates	≤ 30%	Lab duplicate	≤ 20%	≤ 20%
Total organic carbon, TOC	Field duplicates	≤ 30%	MS/MSD or Lab duplicate	≤ 20%	≤ 17.8% if ≤ 10 mg/l ≤10.8% if > 10 mg/l
Dissolved organic carbon, DOC	Field duplicates	≤ 30%	MS/MSD or Lab duplicate	≤ 20%	≤ 17.8% if ≤ 10 mg/l ≤10.8% if > 10 mg/l
Tannins and Lignin	Field duplicates	≤ 30%	MS/MSD or Lab duplicate	≤ 20%	NA
Total phosphorus, TP	Field duplicates	≤ 30%	MS/MSD or Lab duplicate	≤ 20%	≤ 25.8% if ≤0.8 mg/l ≤9.5% if >0.8 mg/l
Total Soluble Phosphorus, TSP	Not estimated	NA	MS/MSD or Lab duplicate	≤ 20%	≤ 25.8% if ≤0.8 mg/l ≤9.5% if >0.8 mg/l
Soluble Reactive Phosphorus, SRP ("Orthophosphate, dissolved")	Not estimated	NA	MS/MSD or Lab duplicate	≤ 20%	≤ 27.2% if ≤0.4 mg/l ≤11.2% if >0.4 mg/l
Total Reactive Phosphorus, TRP, ("Orthophosphate, total")	Field duplicates	≤ 30%	MS/MSD or Lab duplicate	≤ 20%	≤ 27.2% if ≤0.4 mg/l ≤11.2% if >0.4 mg/l
Ammonia, total, NH_3	Field duplicates	≤ 30%	MS/MSD or Lab duplicate	≤ 20%	≤ 55.7% if ≤0.2 mg/l ≤22.5% if ≤0.8mg/l ≤17.9% if >0.8 mg/l
Nitrite + Nitrate, $NO_2 + NO_3$,	Field duplicates	≤ 30%	MS/MSD or Lab duplicate	≤ 20%	≤ 34.0% if ≤0.8 mg/l ≤14.8% if >0.8mg/l
Total Kjeldahl Nitrogen, TKN	Field duplicates	≤ 30%	MS/MSD or Lab duplicate	≤ 20%	≤ 27.0 if ≤2.0 mg/l ≤13.3% if >2.0 mg/l
Soluble Kjeldahl Nitrogen	Not estimated	NA	MS/MSD or Lab duplicate	≤ 20%	≤ 27.0 if ≤2.0 mg/l ≤13.3% if >2.0 mg/l

Bias in monitoring design

Sample locations are selected based on existing monitoring locations and specific monitoring goals. As such, the data collected are meant to be representative of the locations identified and the cumulative effect of upstream processes. Use of the data to infer average conditions along the length of the tributaries or to any other end may result in biased interpretations.

[1] Calculated according to Standard Methods 1020 (2005) and represents a range of 3 standard deviations or an approximately 99.7% confidence interval (99.7% of all duplicate sample pairs should have an RPD within this range).

Other sources of bias include the following:

- Sampling only in daylight and at different times of the day from one sampling event to the next may affect some parameters which fluctuate on a daily time scale (notably temperature and dissolved oxygen, but possibly others as well).
- Extreme or unusual conditions, such as storm events, may not be sufficiently sampled due to field staff safety concerns, station inaccessibility, and the infrequent nature of such events.
- Sampling locations are often located at bridge crossings due to ease of access. Sampling occurs on the upstream side of the bridge whenever possible to minimize impacts, but the actual effect of bridges on ambient water quality is unknown. Sampling may occur on the downstream side of a bridge if there are concerns about traffic safety, debris accumulating on bridge supports or high flow situations (safety of sampling equipment or probe immersion).

Applying consistent sampling methods, SOPs, and analytical methods will minimize bias from other sources.

Representativeness

Tributary sampling locations have been selected, where possible, such that they have sufficient flow year-round to allow for sampling of well-mixed areas of the waterbody. This allows the samples to represent the average condition of the waterbody at that point in time. In the event that a sampling location does not have sufficient flow on a given sampling date to obtain a representative sample, field staff will advise the Project Manager. Samples will not be collected from tributaries when water is stagnant.

Comparability

The objective for comparability is to have data which are comparable between sampling locations as well as comparable over time. Comparability is promoted by

- Fixed station locations
- The use of standard U.S. EPA approved methods where possible
- Consistent application of SOPs detailed in the QAPP and its appendices
- Consistent application of analytical methods specified in the QAPP
- Achieving the required practical quantitation limits detailed in the QAPP
- Use of data reporting qualifiers for samples not achieving the QA/QC criteria specified

Completeness

It is expected that some site visits or samples will be missed due to problems such as inclement weather, temporary station inaccessibility, equipment problems, and staffing issues such as illness. Many of these impediments are unavoidable. In the event of a missed sample, the Field Supervisor should contact the Project Manager to discuss options for obtaining the sample and to discuss whether long-term changes to the sampling program are necessary.

A.8 Special Training/Certification

Field staff

Field staff will be contracted from a Division of Water Resources (DWR) certified field lab (Environment 1, Inc.) and the lab must maintain their certification for the duration of their monitoring contract. Inherent in the annual recertification process are acceptable results for proficiency testing for all applicable parameters. In addition, field staff routinely collect data as part of the State's Monitoring Coalition Program and, as part of that program, the DWR Monitoring Coalition Coordinator routinely audits and trains field staff on ambient sampling methods. Field staff will be provided copies of the SOPs and this QAPP and these will be available to field staff at all times.

Laboratory (analytical) staff

Analyses will be conducted at laboratories that are certified by the DWR wastewater/groundwater laboratory certification program, and staff training will be performed in accordance with the requirements inherent in this certification. All laboratory personnel receive training and have proven proficiency in their designated analytical procedures. Laboratory personnel will be provided copies of the appropriate SOPs and this QAPP and these will be made available in the laboratory at all times. The laboratory must maintain certification for parameters being sampled under this program, where available. Certification may come from either DWR or the NC State Laboratory of Public Health (NC Department of Health and Human Services, Division of Public Health). Parameters requiring certification and the certifying authority are listed in Table B.1.3. In the event that the laboratory loses certification for any parameters, it will be laboratory's responsibility to find an alternate certified laboratory and to contract that lab to conduct those samples under the QA/QC requirements of this QAPP.

A.9 Documents and Records

Quality assurance information, SOPs, and other support documentation

Once all approval signatures have been obtained, the QA Manager will electronically distribute copies of the approved QAPP to persons on the distribution list in Section A3 of this document. Copies will be disseminated within 30 days of notification of final approval. The original hard copy with approval signatures will be kept on file in the QA Manager's office at Cardno.

The QA Manager is to be notified of changes made to SOPs, analytical methods, or any other documentation referenced by this QAPP by the field and laboratory staff at Environment 1, Inc. The QA Manager will then be responsible for distributing the information, as described above. The QA Manager will also be responsible for keeping current copies of these documents on file at Cardno. The QA Manager will periodically (at least annually) check with appropriate staff at DWR to determine if DWR has made any changes to the SOPs referenced in the Appendices to this QAPP. The QA Manager will then assess whether those changes are material to this QAPP and will recommend a course of action to the Project Manager.

For the duration of the UNRBA data collection project, this QAPP will be reviewed on at least an annual basis and, if appropriate, changes or updates will be made at that time. However, critical revisions can

be made at any time. The QA Manager is responsible for completing revisions, obtaining signatures of approval, and disseminating the revised document to those on the distribution list within 30 days of final approval. Changes to the Appendices of this QAPP do not constitute changes to this QAPP and will not necessitate resubmission to and re-approval by DWR. Changes to the Monitoring Plan which do not affect the suite of SOPs, methods, and quality assurance criteria documented in this QAPP will not necessitate re-approval of this QAPP by DWR. Addition of parameters to the Monitoring Plan which are being collected to support modeling under the Falls Lake Rules will require revisions to this QAPP which will then be resubmitted to DWR for approval. The addition of parameters to the monitoring plan which fall outside the scope of the Falls Lake Rules will not necessitate the resubmission and re-approval of this QAPP.

Revisions to this QAPP will be tracked by version numbers and approval date which shall be easily identifiable by the document control information on each page. A complete list of all revisions/updates will be maintained at the beginning of the document, beginning with the first DWR-approved version.

Project Records

The records produced during this project, their location, retention time, format, and disposition at the end of the required retention time are summarized in Table A.9.1

Field data collection forms.

Field log sheets serve as a daily record of events, observations, and measurements during all field activities. Field staff will record all relevant information relating to sampling activities on the field log sheets. Field data will be transcribed and reviewed by field staff and uploaded to the UNRBA data management system as described in sections A.6, B.10, and D of this QAPP.

Entries on the field log sheet will include:

- Names of the field crew
- Date
- Sampling start time
- Location of sampling activity
- Sampling method
- Sampling equipment used
- Type of samples collected
- Date and time of each sample collection
- Sample identification numbers
- Preservatives used
- Field measurements
- Field observations and details related to analysis or integrity of samples (e.g. weather conditions, noticeable odors, colors, etc.)
- Qualitative stream-flow description or rating

Field meter calibration sheets will be used to record daily meter calibrations, standard solutions and concentrations used, and all readings from post-calibration checks and any recalibrations of the instruments during the day.

Electronic copies (e.g. scanned pdf files) of the field data sheets and field calibration logs will be uploaded to the UNRBA's electronic document management system monthly. Hard copies will be organized and archived by Environment 1, Inc. and will remain available at the Environment 1 offices for review by members of the project team for a period of 5 years following the conclusion of the monitoring program.

Photographs

Photographs will be taken at the sampling locations for each site visit when samples are collected. These will serve to verify the site and conditions present during sampling. At a minimum, a photograph should be taken at the sampling location looking in the upstream direction. Additional photographs may be taken at each site to document conditions at the discretion of the field staff. For each photograph taken, the following information should be recorded on the field data log sheet:

- Time, date, location, direction of photograph, weather conditions
- Description of the subject photographed (e.g. upstream, downstream, note deer carcass, etc.)
- Name of person taking photograph
- Photograph identification numbers

Whenever possible, photos should be taken with a device capable of storing time, date, and location metadata with the photograph. This data can serve as a QA check that samples were collected at the correct location as well as providing a visual reference of the conditions at the site in the event that questionable results are obtained. Review of photographs and their metadata will not be a routine part of QA/QC procedures for each monitoring event, but will provide the ability to spot-check as necessary.

Photographs will be uploaded to the UNRBAs document management web site monthly.

Table A.9.1. Project records, format, and retention time. The countdown clock for all retention times begins at the conclusion of the monitoring program—not on the date each individual document is created.

Document	Minimum Retention Time (following conclusion of project)	Format	Disposition
Field Staff. Location: Staff office.			
Meter calibration sheets	5 years	hard copy	Discard
Field data sheets – hard copy	5 years	hard copy	Discard
Field data – electronic	5 years	comma delimited text files	Discard
Staff notes	5 years	hard copy	Discard
Photographs	5 years	electronic (e.g. jpg)	Discard
Courier logs (where applicable)	5 years	hard copy	Discard
Project Manager. Location: Cardno			
Data review notes	10 years	hard copy / electronic	Discard
Audit reports, field and lab	5 years	hard copy / electronic	Provide to UNRBA
Database Manager. Location Cardno			
Master database	10 years	PostgreSQL	Provide electronic archive to UNRBA
Field and laboratory data – electronic submissions from field and laboratory staff	10 years	comma delimited text files	Archive electronically, provide to UNRBA
Electronic copies of field notes, photographs, data reports, etc.	10 years	electronic files, e.g. *.pdf, *.jpg, etc.	Archive electronically, provide to UNRBA

Electronic data storage

All field measurements and observations, site visit comments, and analytical results (including data qualifiers) are ultimately warehoused in a PostgreSQL database. Copies of this warehouse reside on the Cardno server and backups will be made on a daily basis and stored for a period of 30 days. Copies of monthly backups will be archived for a minimum of 10 years. The database will be stored in a minimum of two physical locations: currently, one in the Cardno office in Raleigh, North Carolina and the other in Cardno's Austin, Texas, datacenter. Details of electronic data management and warehousing methods are further described in section *B.10: Data Management*.

Data Reporting

Annual reports will be submitted to the UNRBA in April of each year with data included at least through December of the prior year. This report will include summaries of data collected at monitoring locations, analysis of deviations of samples from expected values, and recommendations for sampling in the following fiscal year. The report may include further analyses as agreed upon by Cardno and the UNRBA.

Interim reports submitted in October of each year (December in Year 1) will include a data assessment report (description of data format, method codes, station codes, qualifier codes, and any known quality assurance or other issues) along with metadata summaries of data collected, results of field and lab audits as appropriate, and other related information.

The UNRBA data will be provided annually to the DWR in the format used by the Division of Water Resources' Monitoring Coalition Program for monthly data submissions. The use of this data specification will ensure that data are submitted in a format that DWR routinely processes.

SECTION B — **DATA GENERATION & ACQUISITION**

B.1 Sampling Process Design

Overview

The UNRBA monitoring program is designed to monitor water quality in tributaries entering Falls Lake, at select jurisdictional boundaries throughout the watershed, and, if deemed necessary, at locations within Falls Lake to supplement data being collected by DWR. Sampling locations and sample frequency are selected based on existing data and the current understanding of loading from each tributary and its influence on Falls Lake water quality as predicted by the DWR Falls Lake Nutrient Response Model. These sites and sample frequencies are meant to be adaptive and are subject to change. The initial monitoring plan is provided as Appendix 1. The Project Manager will keep a current list of all monitoring locations, frequencies, and parameters to be sampled, along with a historical record of any changes made to this plan.

Station Locations

Sample locations are located at fixed locations (i.e. specific latitude and longitude). Tributary locations are selected so that they are publically accessible, generally at bridge crossings, and so that they are representative of tributaries even under high water conditions (e.g. they do not transition between lotic and lentic conditions under the normal range of Falls Lake water levels). Tables of initial sample locations are included in Appendix 1 and may change in future years of the monitoring program. The Project Manager will maintain a current list of all sampling stations and will be responsible for assuring field staff are aware of any changes to monitoring locations.

Field monitoring staff should make all reasonable attempts to:

- Conduct sampling and monitoring as consistently as possible at the same location in order to reduce unknown sources of variation.
- Sample tributaries in the main stream channel in an area of well-mixed flow outside of any discharge mixing zones.
- Use best professional judgment to sample from a fixed location that will introduce the least amount of contamination to the sample.
- Follow the “Bank/Dock Sampling” guidelines of the DWR ISB SOP (Appendix 3) if site conditions require that sampling occur from these locations.
- Notify the Project Manager within 48 hours of any sites that are sampled from locations other than those specified.
- Document temporary changes to sampling locations caused by safety concerns, accessibility, and stream flow patterns, on the field sheet and in the comments section of the data submittal sheet.
- Inform the Project Manager within one week if future sampling is expected to be prevented or its location altered due to accessibility or safety concerns.

Site Verification

At least once per year, and during each individual’s first sampling event at each site, field staff should record GPS coordinates in decimal degrees to at least the fourth decimal place (DD.DDDD) and verify the GPS coordinates against the values listed in the Monitoring Plan (Appendix 1). The Project Manager

should be notified of any inconsistencies. On their first site visits, new field staff are expected to confirm the field coordinates at each sampling location with a GPS device. GPS coordinates are expected to match the values identifying sampling locations to at least the first three decimal places.

In addition, photographs will be taken for each site at each monitoring visit. These photographs may be used to verify sites at which samples are collected.

Trespassing

Sites have been selected to be publicly accessible. In no case is trespassing on private property permitted when accessing sampling sites. This includes parking in private driveways.

Parameters measured

Parameters to be measured vary by the category of sampling site and the initial list of parameters to be measured for each site is provided in Appendix 1. Table B.1.3 is a list of all parameters that may be measured under this QAPP and identifies the sampling SOP to be followed for each.

Sampling and measurements

Field measurements and samples are taken in accordance with Sections III and IV of the DWR ISB SOP Version 2.1 (December 2013) (Appendix 3) and the DWR Wastewater/Groundwater Laboratory Certification Approved Procedures for Field Analysis, revised April 2013 (Appendix 2). Samples related to specific UV absorbance (SUVA) are collected according to EPA Method 415.3 (Appendix 4).

Required sample volumes, containers, preservation, and sample handling requirements are summarized in Table B.2.1. After collection and chemical preservation, samples are stored immediately on ice in coolers. The coolers are delivered by field staff to the laboratory.

If samples arrive at the laboratory in unacceptable condition (e.g., temperature out of range, inadequate chemical preservation) they can be rejected by laboratory staff. Resampling for these discarded samples should be performed as soon as possible and within 2 days for sites sampled weekly, 5 days for sites sampled monthly, and 10 days for sites sampled quarterly.

Sample Spacing

Samples defined as twice monthly shall be collected with no less than 10 and no more than 21 days between sampling events. Monthly samples should be collected with 23 to 36 days between samples. Quarterly samples should be collected with 80 to 100 days between samples.

All monthly jurisdictional boundary and lake-loading stations should be monitored within a 10 business-day period. Data should be collected at all lake-loading sites within a single 5 day period. The 5 lake loading stations with the largest drainage areas (Ellerbe Creek, Eno River, Little River, Flat River, and Knap of Reeds Creek) should be sampled on the same day. The second sample for the lake-loading stations with twice per month sampling should be collected on the same day at all locations between 10 and 21 days after the first sample of the month. All sites that are sampled quarterly should be sampled within a single 10-day period.

Table B.1.3. Water quality parameters which may be measured as part of the UNRBA monitoring program along with sampling SOP. Actual measurements collected may include a subset of these parameters, per the Monitoring Plan in Appendix 1.

Parameter	STORET Code	Sampling SOP	Certifying Authority
Field Parameters			
Water temperature (^oC)	00010	DWR WW/GW, April 2013.[1]	DWR
Specific conductance (µS/cm at 25^oC)	00094	DWR WW/GW, April 2013.	DWR
Dissolved oxygen (mg/L)	00300	DWR WW/GW, April 2013.	DWR
pH (standard units, SU)	00400	DWR WW/GW, April 2013.	DWR
Air temperature (^oC)	00020	DWR WW/GW, April 2013.	N/A
Turbidity (NTU)	82078	EPA 180.1 Revision 2.0	N/A
Instantaneous Discharge (CFS)	00061	ISB SOP Version 2.1	N/A
Secchi depth (m, lake sites only)	00078	ISB SOP Version 2.1	N/A
Samples for Lab Analysis			
Total suspended solids, TSS (mg/L)	00530	ISB SOP Version 2.1	DWR
Turbidity (NTU)	82079	ISB SOP Version 2.1	DWR
Chlorophyll *a* (µg/L)	70953	ISB SOP Version 2.1	DWR
5-day carbonaceous biochemical oxygen demand, $CBOD_5$ (mg/L)	80082	ISB SOP Version 2.1	DWR
5-day biochemical oxygen demand, BOD_5 (mg/L)	00310	ISB SOP Version 2.1	DWR
Color (Pt-Co units)	00080	ISB SOP Version 2.1	DWR
UV absorbance at 254nm (cm^{-1}) (for SUVA)	NA	EPA 415.3 / SM 5910B	SLPH
Visible absorbance at 440 nm, (cm^{-1})	NA	Same sample as UV absorbance.	N/A
Carbon			
Total organic carbon, TOC (mg C /L)	00680	ISB SOP Version 2.1	DWR
Dissolved organic carbon, DOC (mg C /L)	00681	EPA 415.3	DWR
Nutrients			
Total phosphorus, TP (mg P /L)	00665	ISB SOP Version 2.1	DWR
Total Soluble Phosphorus, TSP (mg P /L)	00666	ISB SOP Version 2.1	same as TP
Total Reactive Phosphorus, TRP, Orthophosphate, total[2] (mg P /L)	00660	ISB SOP Version 2.1	DWR
Soluble Reactive Phosphorus, SRP, Orthophosphate, dissolved[3] (mg P / L)	00671	ISB SOP Version 2.1	same as TRP
Ammonia, total, NH_3 (mg N / L)	00610	ISB SOP Version 2.1	DWR
Nitrite + Nitrate, $NO_2 + NO_3$ (mg N / L)	00630	ISB SOP Version 2.1	DWR
Total Kjeldahl Nitrogen, TKN (mg N /L)	00625	ISB SOP Version 2.1	DWR
Dissolved Kjeldahl Nitrogen, (mg N / L)	00623	ISB SOP Version 2.1	same as TKN

[1] DWR Wastewater/Groundwater Laboratory Certification Approved Procedures for Field Analysis, revised April 2013.
[2] unfiltered, also referred to as total reactive phosphorus (TRP)
[3] filtered, also referred to as soluble reactive phosphorus (SRP)

Missed samples

Occasional extreme events may prevent sampling from occurring according to the schedule prescribed above. Under those circumstances, any missed samples should be collected when safe conditions return and the original monitoring schedule should be resumed for subsequent sampling events.

Every reasonable attempt is to be made by field staff to complete all scheduled site visits; some missed visits are to be expected due to situations including, but not limited to, extreme weather, station inaccessibility, extreme flow (either low flow which makes sampling impossible or inappropriate due to pooling/backwaters, or flooding preventing access of normal sampling point), and meter problems. In these cases, the Project Manager should be notified within 2 days. The first missed event at any site due to lack of flow or site inaccessibility will be treated as a missed sample and a second sampling attempt will not be made. In this case, conditions will be evaluated by the Project Manager and discussed with Environment 1, Inc. to assess whether changes to the Monitoring Plan are necessary. Missed samples due to factors such as illness or extreme weather should be discussed with the Project Manager and arrangements made to resample the location as soon as practicable. Longer-term inaccessibility, most notably due to bridge construction, should be assessed by the Project Manager for consideration of temporary suspension or relocation of the station. It is important that stations not be moved without sufficient reason, as an uninterrupted long-term record is one objective of this program.

B.2 Sampling Methods

Overview

Samples and measurements for most parameters are to be taken in accordance with the North Carolina Department of Environment and Natural Resources Division of Water Resources' Intensive Survey Branch Standard Operating Procedures (ISB SOP) (Appendix 3) and the approved procedures for the analysis of field parameters from the wastewater/groundwater laboratory certification program (Appendix 2). In addition, samples and measurements of parameters not measured by DWR (e.g. specific UV absorbance, SUVA, and field turbidity measurements) will follow existing EPA methods (Appendix 4). Any irregularities or problems encountered by field staff should be communicated to the Project Manager, either verbally or via email. The Project Manager will assess the situation, consult with other project personnel if needed, and recommend a course of action for resolution.

Field measurements - Tributaries

Field measurements at tributary locations are to be taken just below the water surface (depth between 0.10 and 0.15 m). Temperature and dissolved oxygen shall be measured *in situ* whenever possible according to the methods of DWR WW/GW Laboratory Certification Program's Approved Methods for the Analysis of Field Parameters (Appendix 2). In the event that safety concerns prevent *in situ* sampling (e.g. highway bridge crossings, etc.) grab samples may be collected and measurements made immediately in a safe location according to the same DWR guidance documents. Specific conductivity and pH measurements may be made using grab samples.

Sample collection - Tributaries

At tributary locations, samples for the parameters listed in Table B.1.3 will be obtained as grab samples just below the water surface (depth between 0.10 and 0.15 m). Samples will be collected using a bridge sampler on the upstream side of the bridge where possible or an approved intermediary device when samples are collected from a bank. An intermediary device may be used from a bridge if the water depth is not deep enough to accommodate a bridge sampler. When used, an intermediary device must be rinsed three times using water from the sampling location prior to obtaining the sample. Sample sizes and bottle types for each analysis are provided in Table B.2.1

Field measurements – Falls Lake

Measurements of temperature, pH, dissolved oxygen, and conductivity for lake samples will be made at discrete depths (from the surface to 10 m at 1m increments and at least every 5 m thereafter).

Sample collection – Falls Lake

At lake locations, samples will be collected as photic zone composites. These samples will be a composite sample over the entire depth of the photic zone, calculated in the field as twice the Secchi depth, and will be collected using a Labline® Poly-Pro water sampler or similar depth-integrating sampling device. If using a Labline sampler, corks are removed from the device and it is then slowly lowered to a depth of twice the Secchi depth and then drawn back up to just below the surface. Lowering and raising the sampler is done at a slow and continuous pace in order to fill the sampler with a representative sample of the photic zone water column. If the photic zone is less than 1 m, samples may be taken as grab samples just below the water surface (depth ≈ 0.15m). Secchi depth should be measured according to the DWR ISB standard operating procedures (Appendix 3).

Although not routinely collected, discrete depth samples may be collected as part of a special study. In these cases, samples will be collected using a Labline or Van Dorn type sampler which is lowered to a specified depth and triggered as appropriate to collect the water sample.

Sample sizes and bottle types for each analysis are provided in Table B.2.1

Table B.2.1. Sample sizes, bottle types, holding conditions, and preservation for samples included in the monitoring program.

Analyte (unit)	Volume (ml)	Bottle Type (P = plastic)	Filter in Field?	Holding Temp. (°C)	Maximum Holding Time (d)	Preservative	Target pH
Total suspended solids, TSS	1000	P (disposable)	No	≤ 6	7	None	N/A
Turbidity	200	P (disposable)	N/A	≤ 6	2	None	N/A
Chlorophyll *a*	500	P (brown, wide mouth)	In lab within 24 hours	≤ 6 before filtering ≤ -20 after filtering	24 after filtering	None	N/A
Carbonaceous Biochemical Oxygen Demand ($CBOD_5$)	1000	P (disposable)	N/A	≤ 6	2	None	N/A
Biochemical Oxygen Demand (BOD_5).	1000	P (disposable)	N/A	≤ 6	2	None	N/A
Total organic carbon, TOC	200	P (disposable)	N/A	≤ 6	28	H_2SO_4	< 2
Dissolved organic carbon, DOC	200	P (disposable)	In lab within 48 hours	≤ 6	28	H_2SO_4, after filtration.	< 2
UVA-254 (absorbance at 254 nm)	200	G-amber	No	≤ 6	2	None	N/A
Color (Pt-Co units)	* same sample as UVA						
Abs-440 (absorbance at 440 nm)	* same sample as UVA						
Total phosphorus, TP	500	P (disposable)	N/A	≤ 6	28	H_2SO_4	< 2
Total soluble phosphorus, TSP	200	P (disposable)	Yes	≤ 6	28	H_2SO_4	< 2
Total reactive phosphorus, TRP, "Orthophosphate, total"	200	P (disposable)	N/A	≤ 6	2	None	N/A
Soluble reactive phosphorus, SRP, "Orthophosphate, dissolved"	200	P (disposable)	Yes	≤ 6	2	None	N/A
Ammonia, total, NH_3	* same sample as total phosphorus						
Nitrite + Nitrate, $NO_2 + NO_3$	* same sample as total phosphorus						
Total Kjeldahl Nitrogen,	* same sample as total phosphorus						
Soluble Kjeldahl Nitrogen	* same sample as total soluble phosphorus						

B.3 Sample Handling and Custody

Sample preservation

Chemical preservation of samples should occur within 15 minutes of collection. Samples should then immediately be placed in coolers with enough ice to ensure that samples are maintained ≤6° C until arrival at the laboratory. The chemical preservatives required for each sample are listed in Table B.2.1. Samples for DOC and UV absorbance may be held on ice and filtered in the lab within 48 hours of collection (per EPA method 415.3). Immediately after filtration (within 15 minutes), the DOC samples should be acidified and may be stored ≤6° C for up to 28 days from the time of collection. Samples for UV absorbance and color should not be acidified and should be analyzed within 48 hours of collection. Maximum holding times for all samples are provided in table B.2.1.

Sample Handling and Transport

Most samples will be both collected and analyzed by Environment 1, Inc. In some instances, samples may be collected by an organization not affiliated with the laboratory (e.g. City of Durham, City of Raleigh, NCSU Center for Applied Aquatic Ecology, DWR) but transferred to the laboratory for analyses. In other cases, samples may be collected by Environment 1, Inc., but provided to DWR for analysis (e.g. split samples). Assuring sample integrity from collection through analysis will be achieved through appropriate sample labeling and documentation and laboratory submission sheets. Communication between field staff and laboratory staff will be maintained so laboratories know when to expect samples and are prepared to receive and process them appropriately.

Each batch of samples will be accompanied by log sheets containing the following sampling information: unique identification number, sample date and time, sample description, sample preservation (if any), sample preservation time, and the analyses required.

Pre-printed Adhesive Labels

A pre-printed adhesive label will be attached to each sample bottle. Each label will carry the following information: Environment 1 account #, client name, station ID (e.g. “FLR-5.0”), Full station description (e.g. “Flat River at Old Oxford Hwy”), preservative (if any), collection date, sample number for that date (if multiple samples are expected to be collected on a given date), collection depth (if other than surface grab), and test code.

Transport

Coolers with samples will be hand delivered by field staff to laboratories. In the case of samples collected by a municipality, DWR, or CAAE for analysis by Environment 1, Inc., arrangements will be made in advance for the timely transfer of samples from the collector to a representative of the laboratory.

Laboratory handling

Laboratory handling will be performed in accordance with the Laboratory's Quality Assurance Manual (Appendix 5) and will be consistent with the guidelines set forth in this section of the QAPP.

The laboratory must have written standard operating procedures (SOPs) for sample custody including:

- Sample receipt
- Sample storage
- Sample tracking

In addition, the laboratory shall have written SOPs for laboratory safety, cleaning of analytical glassware, and traceability of standards used in sample analysis QA/QC.

Sample receipt

The laboratory SOP for receiving and logging in samples shall include documentation of the following:

- presence or absence of sample labels
- sample label identification numbers
- condition of the sample bottles
- verification of agreement or non-agreement of information on receiving documents
- temperature of samples upon receipt
- resolution of problems or discrepancies

Sample storage

Samples are maintained at 4 degrees Celsius and stored in appropriate areas as to prevent sample contamination.

Sample tracking

The laboratory shall have written SOPs for tracking the work performed on any particular sample. Documentation of sample receipt, storage, preparations, and analysis, along with instrument calibration and other QA/QC activities shall be maintained.

B.4 Analytical Methods

Field measurements

In addition to the SOPs identified in Table B.1.3, the instruction manual for the appropriate meter should be consulted for all field measurements. Reporting levels for all field measurements are provided in table B.4.1 below.

Table B.4.1. Field measurement reporting levels.

Parameter	Reported to nearest
Dissolved oxygen (DO)	0.1 mg/L
pH	0.1 SU
Water temperature	0.1 ºC
Specific conductance	1 µS/cm
Air temperature	1°C
Secchi depth (lake samples only)	0.1 m

Lab analyses

A summary of the methods and PQLs (the laboratory's minimum reporting limit) to be used are listed in table A.7.1. The laboratory's Quality Assurance Manual is provided as Appendix 5 and all relevant laboratory SOPs for the project are included in Appendix 6.

B.5 Quality Control

Field activities

Current QC practices in place for field measurements include meter calibrations and standard checks, which are covered in Section B7: *Instrument Calibration & Frequency* of this QAPP.

Field-duplicate samples of lab-analyzed parameters will be collected at approximately 10% of the stations being sampled each month. Given the initial monitoring plan, two sites from the set of lake loading stations and two sites from the set of jurisdictional boundary locations will be selected for duplicate sampling each month. The duplicates for the lake loading sites will be collected as follows: each month 1 of the 5 largest tributaries will be selected for duplicate samples (Ellerbe, Eno, Little, Flat, and Knap of Reeds) and one of the remaining 13 sites will also be selected. In this way, each of the largest 5 tributaries will have duplicate samples collected at least twice per year, and each of the remaining tributaries will have duplicate samples collected approximately once per year. Two sites will be selected at random (without replacement) from the set of jurisdictional boundary sites for duplicate samples.

In addition to annual proficiency testing as required under the North Carolina Groundwater/Wastewater Laboratory Certification procedures, split samples may be conducted with DWR on a regular basis. Split sample scheduling will be determined in collaboration with DWR per DWR's Study Plan for the Ongoing Assessment of Falls of the Neuse Reservoir, Version 2 (NC-DENR 2011). Acceptance criteria for split samples are discussed in section A.7.

Proficiency for chlorophyll *a* analyses will be determined through DWR's annual chlorophyll *a* round robin. Environment 1, Inc. must participate in the annual round robin and achieve results within the acceptable range calculated using the NELAC Proficiency Testing (PT) method, EPA/600/R-04/003 or alternative method specified in the annual round robin final report.

Equipment blanks will be collected at a frequency of 10% to evaluate whether contaminants have been introduced into the samples during the sample collection due to exposure from ambient conditions or from the sample containers themselves. Blank samples should be collected from a final deionized water rinse of the specified equipment after the equipment has been cleaned in accordance with appropriate cleaning procedures per standard operating procedures (Appendix 3). Blanks must be treated in the same manner as surface water samples, including handling, preservation, and hold times and will be submitted to the laboratory with a separate identification number.

Field filter blanks will be collected for each day of sampling when field filtering occurs (i.e. total soluble phosphorus, soluble reactive phosphorus, or soluble Kjeldahl nitrogen; DOC will be filtered in the lab within 48 hours, per EPA method 315.3). Additional blanks and QA/QC checks will be conducted on a variable basis as part of a field and lab audits, when problems with contamination are suspected, or to assess changes in methods, preservatives, or equipment that are being considered.

If target analytes are found in the equipment or filter blanks, sampling and handling procedures will be reevaluated and corrective actions taken. These may include obtaining sampling containers from new sources, training of personnel, discussions with the laboratory, invalidation or qualification of the results, or other procedures considered appropriate.

Field meters will be calibrated at the beginning of each field day according to manufacturer's instructions and calibrations will be checked after approximately four hours and again after the last sample of the day. Quality control criteria for field meters are provided in section A.7.

Laboratory activities

Required quality control checks for analytical samples will be conducted according to the laboratory's Quality Assurance Manual (Appendix 5) and as specified in section A.7 of this QAPP. The following elements are part of the standard laboratory quality control practices:

- Analysis of method blanks
- Analysis of laboratory control samples (LCS)
- Instrument calibration (including initial calibration, calibration blanks, and calibration verification)
- Analysis of matrix spikes (MS)
- Analysis of duplicates and matrix spike duplicates (MSD)

Quality control objectives and criteria for acceptance for each analysis are presented in Tables A.7.2: *QA Targets for Accuracy* and A.7.3: *QA Targets for Precision*.

Method Blanks

A method blank is an analyte-free matrix, analyzed as a normal sample by the laboratory using normal sample preparation and analytical procedures. A method blank is used for monitoring and documenting background contamination in the analytical environment. Method blanks will be analyzed at a frequency of one per sample batch (or group of up to 20 samples analyzed in sequence using the same method). Corrective actions associated with exceeding acceptable method blank concentrations include isolating

the source of contamination and re-digesting and/or re-analyzing the associated samples. Blank contamination will be noted in the laboratory reports, but sample results will not be corrected for blank contamination. Corrective actions will be documented in the laboratory report's narrative statement.

Laboratory Control Samples

Laboratory control samples (LCS) are laboratory-generated samples analyzed as a normal sample using normal sample preparation and analytical procedures. An LCS is used to monitor the day-to-day performance (accuracy) of routine analytical methods. An LCS is an aliquot of clean water spiked with analytes of known concentrations corresponding to the analytical method. The LCS is used to verify that the laboratory can perform the analysis on a clean matrix within QC acceptance limits. Results are expressed as percent recovery of the known amount of the spiked analytical parameter.

One LCS is analyzed per sample batch. Acceptance criteria (control limits) for the LCS are defined by the laboratory and summarized in Tables A.7.2 and A.7.3 for each parameter. In general, the LCS acceptance criteria recovery range is 80 to 120 percent of the known amount of the spiked analytical parameter. Corrective action, consisting of a rerunning of all samples in the affected batch, will be performed if LCS recoveries fall outside of control limits. Such problems will be documented in the laboratory report's narrative statement.

Matrix Spikes

Matrix spikes (MS) are prepared by adding a known amount of the analyte of interest to a sample. MS are used as a similar function as the LCS, except that the sample matrix is a real time sample rather than a clean matrix. Results are expressed as percent recovery of the known amount of the spiked analytical parameter. Matrix spikes are used to verify that the laboratory can determine if the matrix is causing either a positive or negative influence on sample results.

One matrix spike is analyzed per sample batch. Acceptance criteria for the MS are defined by the laboratory and summarized in Tables A.7.2 and A.7.3. In general, the MS acceptance criteria recovery range is 80 to 120 percent of the known amount of the spiked analytical parameter. Generally, no corrective action is taken for matrix spike results exceeding the control limits, as long as the LCS recoveries are acceptable.

Laboratory Duplicates

A laboratory duplicate is a laboratory-generated split sample used to document the precision of the analytical method. Results are expressed as relative percent difference between the laboratory duplicate pair.

One laboratory duplicate will be run for each laboratory batch or every 20 samples, whichever is more frequent. Acceptance criteria for laboratory duplicates are specified in the laboratory QA Manual and SOPs and are summarized in Tables A.7.2 and A.7.3. If laboratory duplicates exceed criteria, the corrective action will be to repeat the analyses.

B.6 Instrument Testing, Inspection, and Maintenance

Field equipment

Field staff are responsible for regular cleaning, inspection, and maintenance of assigned equipment. All equipment should be visually inspected prior to use for damage or dirt, and repaired or cleaned if needed. If meters are stored for long periods (> 1 week) without being used, it is recommended that they be calibrated and inspected at least weekly to keep them in good working order. Staff should refer to instruction manuals for manufacturer's recommendations for inspection, maintenance, storage, and repair. Maintenance logs shall be retained to document equipment upkeep and servicing. A log entry shall include:

- Name of person maintaining the equipment
- Date and description of the maintenance procedure
- Date and description of any equipment problems
- Date and description of action taken to correct the problems
- List of follow-up activities after the maintenance is complete
- Date the next maintenance or equipment check will be needed

Laboratory analytical equipment

Laboratory analytical equipment will be maintained, inspected, and tested according to manufacturer's recommendations and accepted standard operating procedures for the selected analytical methods and the laboratory's QAM and SOPs (Appendix 5). Logs of instrument maintenance activities shall be kept in the lab and remain available for review by project team members.

B.7 Instrument Calibration and Calibration Frequency

Field meters

All field meters are to be inspected and calibrated at a minimum at the beginning and end of each day used. All field meter calibrations will be re-checked after every four hours of use and quality assurance criteria for these calibration checks are provided in section A.7. Field staff should record calibration information on a field meter calibration log sheet (e.g. Log Sheet for YSI 556MPS, Appendix 6) which includes staff name, date/time of initial calibration and post-sampling check, and meter number. The specific calibration procedures are documented in Appendices 1-4 of the Intensive Survey Branch's SOP and in the manufacturers' instruction manuals. For specific conductance a single point calibration will be used. A three-point calibration will be performed for pH. DO meters should be calibrated using the moist-air calibration method.

Standards should be selected so that they bracket the range of measurements expected; pH buffers (standards) and conductivity standards must be traceable and must not have exceeded their expiration dates. Meters currently in use require pH standards of 4.0, 7.0, and 10.0 S.U.

Meters should also be checked against standards periodically throughout the day and recalibrated if needed if any of the following occur:

- physical shock to meter;
- DO membrane is touched, fouled, or dries out;
- unusual (high or low for the particular site) or erratic readings, or excessive drift;
- extreme readings (e.g., extremely acidic or basic pH; D.O. saturation >120%);
- measurements are outside of the range for which the meter was calibrated.

A post-sampling check is completed at the end of each sampling day to confirm significant drift has not occurred and that readings are accurate and representative. If post-sampling check readings are not within the acceptable QC ranges (DO= ±0.5 mg/L, Specific conductance= ±10%, pH=±0.2) or a post-sampling check is not completed, data are determined questionable and are removed from the dataset. The Project Manager should be notified within 1 business day of any such occurrences to determine whether sampling needs to be repeated.

Laboratory instrumentation calibration

All laboratory instruments will be calibrated according to the recommendations of the manufacturer and accepted procedures associated with the selected analytical methods, SOPs, and the laboratory's QAM (Appendix 5).

B.8 Inspection/Acceptance of Supplies & Consumables

Environment 1, Inc. performs quality assurance of sample bottles, reagents, and chemical preservatives that are provided to field staff. Containers that are purchased as pre-cleaned should be certified by the manufacturer or checked to ensure that the parameters tested are below the published reporting limits. Containers should be stored in a manner that does not leave them susceptible to contamination by dust or other particulates and should remain capped until use. Any containers that show evidence of contamination should be discarded. Certificates for containers certified by the manufacturer should be kept on file by the laboratory.

Additionally, field staff should inspect all bottles before use. Any bottles that are visibly dirty or whose lids have come off during storage should be discarded. It is recommended that field staff periodically check bottles for contamination attributed to storage conditions by filling representative containers with analyte-free water, adding the appropriate preservative(s), and submitting them to the laboratory for wet chemistry analyses. Any container lots showing analyte levels at or above the reporting limits should be discarded.

The chemical preservatives used are provided by the laboratory. Certificates of purity from the manufacturer should be provided when purchased, and these certificates should be kept on file by the laboratory. Any preservatives that show signs of contamination, such as discoloration or the presence of debris or other solids, should not be used and should be discarded. A summary of inspections to be performed by field staff is presented in Table B.8.1.

Table B.8.1. Consumable inspections and acceptance criteria.

Item	*Acceptance criteria*
Sample bottles	• Bottle blanks less than laboratory reporting limits • No visible dirt, debris, or other contaminants
pH standards (4.0, 7.0, 10.0 SU)	• No visible discoloration, debris, or other contaminants • The standards must not be expired.
Conductivity standards (100, 1,000, 50,000 µS/cm)	• No visible discoloration, debris, or other contaminants • The standards must not be expired.
Acid for preservation (sulfuric, phosphoric)	• No visible discoloration, debris, or other contaminants
Distilled or deionized water	• No visible discoloration, debris, or other contaminants
Filters (membrane and glass fiber)	• No visible discoloration, debris, or other contaminants • No rips, missing pieces, or torn margins

B.9 Data Acquisition Requirements for Non-Direct Measurements

The UNRBA may use data collected by DWR, the United States Geological Survey (USGS), the City of Raleigh, the City of Durham, and/or NC State University's Center for Applied Aquatic Ecology (CAAE) which is collected under the respective organizations' QAPPs.

Data collected by the City of Raleigh, City of Durham, or CAAE for the parameters covered in this QAPP will only be used by UNRBA if the lab(s) conducting the analyses are certified by the appropriate certifying agency as listed in Table B.1.3.

Proficiency for chlorophyll *a* analyses will be determined through DWR's annual chlorophyll *a* round robin. Labs producing chlorophyll *a* data which will be used by UNRBA must participate in the annual round robin with results within the acceptable range calculated using the NELAC Proficiency Testing (PT) method, EPA/600/R-04/003 or alternative method specified in the annual round robin final report.

In addition to the proficiency testing requirements associated with laboratory certification and the chlorophyll *a* round robin, split samples may be periodically analyzed with these organizations and DWR if requested by DWR. Split sample scheduling will be determined in collaboration with DWR per DWR's Study Plan for the Ongoing Assessment of Falls of the Neuse Reservoir, Version 2 (NC-DENR 2011). Acceptance criteria for split samples are discussed in section A.7.

In the absence of a DWR-approved QAPP, data collected by the City of Raleigh, City of Durham, CAAE, or other sources will need to meet DWR data quality requirements and undergo DWR review to evaluate data accuracy, precision and representativeness prior to use for potential regulatory purposes per the DWR data guidelines posted online at http://portal.ncdenr.org/web/wq/ps/mtu/assessment#5 (accessed July 22, 2014).

UNRBA may use stream flow data collected by the USGS, atmospheric deposition data from the National Atmospheric Deposition Program (NADP) and the Clean Air Status and Trends Network (CASTNET), and climate data from the National Oceanic and Atmospheric Administration's National

Climatic Data Center (NOAA NCDC) or USGS. UNRBA may use temperature, dissolved oxygen, conductivity, and pH data collected *in situ* from CAAE's Falls Lake platforms in future model calibration or validation. The specific use of these data is not within the scope of this document and will be discussed, if relevant, in modeling quality assurance documents.

Data collected by the outside sources discussed above may be included in the UNRBA data management system, and, if included, will be coded according to the data generating organization so that they can be effectively and easily separated from the data generated under other sections of this QAPP. Additionally, data will be stored with details on the method(s) used along with method detection and reporting limits, where applicable.

B.10 Data Management

Overview

The monitoring program performed under the guidance of this QAPP will produce on the order of 10,000 individual results annually. These results are the combination of field measurements and laboratory analyses across nearly 40 different sampling locations in the Falls Lake watershed. Organized data management is critical to this project.

To facilitate the organized collection of data along with systematic review for quality assurance, the UNRBA will use an environmental data management system. Data will be uploaded by field and laboratory staff into a "holding area" of the data management system prior to review and acceptance of the data into the official database. Several data QA/QC controls will be built into this system to trap errors in data recording and entry and these are described below.

Central to the tracking of data and relating results from a single station visit, is the assignment of a unique visit identifier (VisitID). This VisitID is composed of a site identifier and a date/time identifier. The time identifier associated with this VisitID shall be the arrival time at the site. This VisitID will carry forward through all stages of the data flow process—from the site visit through final entry into the official database.

Field measurements and observations are documented at the time of measurement by field staff on field data sheets. Field staff will upload these results along with any anomalies and other comments and observations using standardized spreadsheets to the Data Management System. Hard copy field sheets will be archived at the field staff office and copies will be electronically uploaded to the UNRBA's document management system for review by the Project QA Manager and Project Manager.

Samples are submitted to the laboratory with the appropriate documentation as described in section B.3 of this document. Analytical results, including data qualifier codes, are uploaded to the Data Management System in standardized excel spreadsheets. The laboratory will keep all bench sheets on file and will make them available for review for a period of at least five years from the completion of the monitoring program. In addition, full laboratory analytical and quality control reports will be uploaded by Environment 1, Inc. to the UNRBA's Document Management System for each monitoring event. These reports will include the following, as appropriate:

- Case narrative, including a statement of the conditions in which samples were received, description of any deviation from standard procedures, explanation of any data qualifiers used, and identification of any problems encountered during analysis.
- Computer generated report form containing all sample results

The Quality Assurance Manager will review uploaded files for errors and omissions. In addition to visual checks of the data, built-in quality assurance checks will alert the Quality Assurance Manager to missing values, out-of-range values, and values which are theoretically possible but substantially different from prior values. After review and any necessary corrections, and a final verification following the procedures in Section D, the data will be appended to the current database which will contain all data collected under this monitoring program from its start in 2014 through the project's termination.

SECTION C — **ASSESSMENT AND OVERSIGHT**

C.1 Assessments and Response Actions

The Project Manager acts as the liaison between the team members involved in data collection and analysis and the UNRBA. Issues with any aspect of the program noted by any member of the project team or management should be reported as soon as possible to the Project Manager who will assess the issue, consult with other parties as needed, and determine the course of action to be taken.

Field and Laboratory Audits

The Project Manager or her designee will accompany field staff on the initial visit to field sites to verify coordinates and address any site access issues. In addition, within two months of hire, new field staff will be observed on a sampling run by the Project Manager or her designee. Experienced field staff will be observed on sampling runs at least once every year. In addition, the Quality Assurance Manager will review previous field records including data sheets, log books, calibration records, and other documents. The main purpose of these assessments is to ensure that field staff are performing activities in accordance with current SOPs and to determine if there are any other issues that need to be addressed. Concerns or irregularities noticed by the reviewer will be discussed with field staff. If significant issues arise, the reviewer will notify the Project Manager, field staff, and the appropriate field supervisor by written memorandum, describing the issue and providing recommendations for correcting the issue. As the direct supervisor of field staff, the field supervisor is responsible for ensuring that these significant issues are resolved.

The laboratory is certified by the DWR laboratory certification program. The laboratory must maintain that certification throughout the duration of their participation in the monitoring program including all required proficiency testing and participation in the DWR sponsored chlorophyll *a* round-robin. If the lab loses certification for any parameters while under contract for this project, the lab will submit samples for parameter(s) in question to a laboratory with current certification for analysis. The Project Manager or her designee will complete a lab audit of the contract laboratory at least annually for the duration of the monitoring program. This audit will be scheduled, if possible, during the analysis of project samples. The audits will include an assessment of all quality system documents as well as the laboratory QAM (Appendix 5) and SOPs (Appendix 6). The audit will include a laboratory site visit and discussions with the Laboratory Director and QA/QC Manager. Also, spot checks will be performed to interview individual analysts with regard to methods used, knowledge of quality systems, training, and competency.

Field Measurements

Prior to each use of monitored equipment (e.g. dissolved oxygen or pH meters), the Field Staff will review previous calibration sheets and address any problems with the sensors prior to their use. The result of each review should be noted on the instrument's calibration sheet. At the conclusion of each monitored event, all calibration sheets will be reviewed by the Environment 1 QA/QC Manager to assess the adequacy of the quality control checks (e.g. post-use calibration checks) and to review the instrument's performance to identify any problems or necessary maintenance.

Field quality control checks consisting of field duplicates, equipment blanks, and filter blanks are analyzed for each sampling event as described in sections B.5 and A.7 of this QAPP. The Environment 1, Inc. QA/QC Manager will review all field QA/QC data after each monitored event (e.g. monthly sampling event) and will assess the adequacy of the quality control checks and identify any problems. The laboratory QA/QC Manager will notify the Project QA Manager in writing of any quality control check issues and to discuss corrective actions.

Laboratory Measurements

The laboratory will perform quality control checks for each analysis as documented in sections A.7 and B.5 of this QAPP. Environment 1, Inc. will provide a monthly summary of all QA/QC results noting any quality control issues and potential problems in the case narrative.

C.2 Reports to Management

Data are analyzed and summarized annually by the Cardno Project Team and submitted to the UNRBA Executive Director in April of each year. This submittal will include all data collected through December of the prior year. This report will include summaries of data collected at monitoring locations and recommendations for sampling in the following fiscal year. The report will also document the results of performance evaluations and audits and data quality assessments. The report may include further analyses as agreed upon by Cardno and the UNRBA.

Interim reports submitted in October of each year (except in Year 1) will include a data assessment report (description of data format, method codes, station codes, qualifier codes, and any known quality assurance or other issues) along with metadata summaries of data collected, results of field and lab audits as appropriate, and other related information.

In addition to these reports, the Project Manager will report any issues of concern to the UNRBA Executive Director as they arise.

SECTION D — **DATA VALIDATION AND USABILITY**

D.1 Data Review, Verification, and Validation

Data verification and validation occurs at every step of data generation and handling. Field staff, laboratory support staff, laboratory chemists, and data entry staff are each responsible for verifying that all records and results they produce or handle are completely and correctly recorded, transcribed, and transmitted. Each staff member is also responsible for ensuring that all activities performed (sampling, measurements, and analyses) comply with all requirements outlined in the following project documents:

- This QAPP
- The SOP documents identified in the QAPP and attached as Appendices 2, 3, and 4
- The laboratory's Quality Assurance Manual (Appendix 5)
- The laboratory's SOPs (Appendix 6)

The Quality Assurance Manager is responsible for final verification and validation of all results.

D.2 Verification and Validation Methods

Data verification and validation activities involve many steps and are performed at multiple stages along the process from sample collection to analysis to reporting. Data verification is done at the field and bench levels, by laboratory reviewers, by the Project Manager, and by the QA Manager.

Field staff

Field staff will visually check the following items as produced to ensure that they are complete and correct:

- Sample labels
- Sample submission documentation
- Field data worksheet (hard copy)
- Electronic field data spreadsheet submission (transcription of hard copy field worksheet)

Field staff will review measurements as they are collected to assess if temperatures, pH, dissolved oxygen, and conductivity readings seem reasonable. They will monitor sample storage in the field to ensure that samples are stored on ice and that temperatures in the cooler are maintained below 6 degrees Celsius by verifying the presence of ice.

Laboratories

Laboratory staff will verify that samples arrived at the lab at the proper storage temperatures and that lab analyses occur within the specified holding times. Individual analysts will verify the completion of their analyses and required bench sheets. The laboratory QA/QC Manager or designee will review calculations and inspect laboratory bench sheets and log books to verify their accuracy, completeness, and adherence to the specified method protocols. Calibration and QC data will be examined daily by the individual analysts. The laboratory QA/QC Manager or designee will verify that all instrument systems

are working within specified guidelines and that the QA objectives for accuracy, precision, completeness, and adherence to the required detection and reporting limits are being met. A summary of all the QA/QC results and any non-conformance issues will be included in the laboratory data report for each monitoring event and uploaded to the UNRBA's document management system.

Data Validation

According to U.S. EPA guidance, data validation is typically performed by someone independent of the project activity and not associated with the organization responsible for producing the dataset. However, the validator needs to be familiar with both the data validation requirements and the project objectives. The Quality Assurance Manager from Cardno will conduct the data validation since Cardno project staff are not directly involved in the field or laboratory operations.

The first step of data validation is to inspect the data and the verification and review records to ensure that no oversights were made during that process. A complete set of field and laboratory information will be provided to the data validator for this task. The planned uploads to the UNRBA's document management system described under section B.10 will provide the necessary documentation for this process.

The primary purpose of the data validation is to evaluate the data against the data quality objectives presented in section A.7 of this QAPP. These objectives include criteria for the accuracy, precision, representativeness, comparability, completion, and compliance with required data reporting limits. The following will be checked as part of the validation procedure:

- field measurements data collection
- field sample collection
- sample custody, transport, and preservation
- laboratory analytical results and case narrative
- data reviews
- quality control data

The QA Manager will conduct a systematic review of the data for compliance with the established quality control criteria based on duplicate, spiked, control, and blank data results provided by the laboratory. In addition, quality assurance evaluations of data accuracy, precision, and completeness will be performed for each monitored event. The data validation qualifiers listed in table D.2.1 will be used when validating the data.

Table D.2.1: Common data qualifier codes (flags)

J	Estimated value; value may not be accurate. J1. Surrogate recovery limits have been exceeded. J2. The reported value failed to meet the established QC criteria for either precision or accuracy. J3. The sample matrix interfered with the ability to make any accurate determination. J4. The data is questionable because of improper laboratory or field protocols. J5. Temperature limits exceeded (samples frozen or >6°C) during transport. Non-reportable for NPDES compliance monitoring. J6. The laboratory analysis was from an unpreserved or improperly chemically preserved sample. The data may not be accurate.
N	Presumptive evidence of presence of material; estimated value. This code is used if: N3. The level of analyte is too low to permit accurate quantification, but the estimated concentration is greater than the laboratory method detection limit, but below the laboratory practical quantitation limit.
P	Elevated PQL due to matrix interference and/or sample dilution.
Q	Holding time exceeded. These codes shall be used if the value is derived from a sample that was received, prepared, and/or analyzed after the approved holding time restrictions for sample preparation and analysis. Q1. Holding time exceeded prior to receipt by lab. Q2.Holding time exceeded following receipt by lab.
U	Indicates that the analyte was analyzed for but not detected above the reported PQL. The value reported with the "U" qualifier is equal to the PQL.
V	Indicates the analyte was detected in both the sample and the associated method blank. Note the values in the blank shall not be subtracted from the associated samples.
X	Sample not analyzed for this constituent. X1.Sample not screened for this compound. X2.Sampled, but analysis lost or not performed- field error. X3.Sampled, but analysis lost or not performed- lab error.
Y	Elevated PQL due to insufficient sample size.
Z	The sample analysis/results are not reported due to: Z1. Inability to analyze the sample. Z2. Questions concerning data reliability. The presence or absence of the analyte cannot be verified.

Project Quality Assurance Manager

Final review, validation, and verification duties of results reported by field staff and the laboratory are performed by the Project Quality Assurance Manager on an ongoing basis.

As received: Review electronic submissions of lab reports and any hard copy lab reports of anomalies. Consult Laboratory staff for clarification or corrections if needed. Review data entry of analytical results.

Monthly: Review electronic field data submissions. Consult individual Monitors for clarification or corrections if needed.
Quarterly: All results, field and analytical, compiled, reviewed, validated, and verified.

When errors or omissions are found or suspected, focused verification will be conducted. The available electronic field data submissions or hard copy lab reports will be consulted to rule out transcription or data entry errors. If no errors are found in these records, the field staff that conducted the sampling/measurement or the appropriate laboratory chemist will be contacted so they can consult original hard copy records. If the result in question is found to be in error as compared to the original documentation, it will be corrected by the QA Manager. In the case of "impossible" values (e.g., pH of 19) if a corrected value cannot be determined from original documentation, the result will be deleted. "Unusual" values (i.e., above or below the latest five year period's minimum or maximum for that station) that are confirmed by original documentation are left intact and unqualified.

Once these steps are completed, data and any accompanying information (comments from field staff, data qualifiers/flags) are considered finalized and are added to the data warehouse.

Data end-users

Questionable data should be brought to the attention of the Project Manager for focused verification. For data collected within the past five years, original lab reports and field data submissions are available from the online Document Management System or in hard copy from the contract laboratory. Field data sheets and hard copy notes will be maintained at the field staff office and laboratory for 5 years following the conclusion of the monitoring program for access as needed. These will be consulted to determine if correction or deletion of any records in the main warehouse is required.

D.3 Reconciliation with User Requirements

The UNRBA will review reports from Cardno annually to assess whether the data collected will meet the anticipated needs of the Association. The monitoring program is designed to be adaptive; monitoring locations, frequency, and parameters can be adjusted as deemed necessary by the Association.

SECTION E — **References**

Cuthbert, I. D., and P. del Giorgio. 1992. Toward a standard method of measuring color in freshwater. Limnology and Oceanography 37:1319–1326.

Mitchell, P. 2006. Guidelines for Quality Assurance and Quality Control in surface water quality programs in Alberta. Report prepared by Patricia Mitchell Environmental Consulting for the Environmental Monitoring and Evaluation Branch of Alberta Environment, Edmonton, Alberta, Canada. July 2006.

NC-DENR. 2009. Falls Lake Nutrient Response Model Final Report. Prepared by N.C. Department of Environment and Natural Resources, Division of Water Quality Planning Section, Modeling/TMDL Unit November 2009.

NC-DENR. 2011. Study Plan for the Ongoing Assessment of Falls of the Neuse Reservoir. Version 2. March 25, 2011. http://portal.ncdenr.org/c/document_library/get_file?uuid=f565bb4f-8428-42f3-93b1-fa701d9d5b59&groupId=38364 (accessed June 16, 2014).

NC-DENR. 2012a. Ambient Lakes Monitoring Program Quality Assurance Project Plan. Version 1.1. July 2012. Prepared by N.C. Department of Environment and Natural Resources, Division of Water Quality, Environmental Sciences Section, Intensive Survey Unit. Raleigh, NC.

NC-DENR. 2012b. Monitoring Coalition Program Field Monitoring Guidance. Version 2.0. December 2012. Prepared by N.C. Department of Environment and Natural Resources, Division of Water Quality, Environmental Sciences Section, Ecosystems Unit, Raleigh, NC.

APPENDICES

Official copies of the Appendices are to be included with this QAPP as a separate electronic or hard-copy document. URLs to documents are provided here where available. These URLs are current as of the date of this document but are subject to change and are not intended to be official archives of these appendices.

APPENDIX 1: UNRBA Monitoring Plan.

APPENDIX 2: NC DENR Approved Procedures for the Analysis of Field Parameters, April 2013.
http://portal.ncdenr.org/web/wq/lab/cert/field/policy

APPENDIX 3: NC DENR Intensive Survey Branch Standard Operating Procedures, Version 2.1 (revised December 2013).
http://portal.ncdenr.org/c/document_library/get_file?uuid=516f1b7b-fbb6-419f-83c8-0c981b2e1f78&groupId=38364

APPENDIX 4: EPA Methods for SUVA
Method 415.3 – Specific Ultraviolet Absorbance (SUVA)
https://www.nemi.gov/methods/method_pdf/7228/
http://www.epa.gov/microbes/documents/Method%20415_3_Rev1_2_Final.pdf

APPENDIX 5: Environment 1, Inc. Laboratory Quality Assurance Manual (QAM)

APPENDIX 6: Environment 1, Inc. Standard Operating Procedures (SOPs)

Appendices

Upper Neuse River Basin Association
Water Quality Monitoring Program

Quality Assurance Project Plan
Version 1.0

July 23, 2014

Contents

Final UNRBA Monitoring Plan

For Submission to the North Carolina Department of Environment and Natural Resources, Division of Water Resources

Approved by DWR July 16, 2014

Cardno ENTRIX
Shaping the Future

Document Information

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DWR_Approved_UNRBA_MonitoringPlan_20140715

Table of Contents

Appendices

Tables

Figures

1 Upper Neuse River Basin Association Monitoring Plan

This monitoring plan was developed jointly by Cardno ENTRIX and the Upper Neuse River Basin Association (UNRBA). Significant input on the monitoring plan was provided by the Path Forward Committee, individual UNRBA members, the UNRBA Executive Director, and technical advisors. Multiple meetings were held with the Path Forward Committee to discuss and revise the monitoring plan. The monitoring plan is also based on a compilation of supporting work conducted by Cardno ENTRIX under contract with the UNRBA over the last two years. The technical memoranda (TM) that document this work include:

Work Completed Under "Support of Long-Term Planning and Regulatory Nutrient Activities in the Falls Lake Watershed" 2012 Contract with UNRBA:

- Task 1 TM: Framework for a Re-examination of Stage II of the Falls Nutrient Strategy. 2013.
- Task 2 TM: Review Existing Data and Reports for Falls Lake and the Watershed. 2012.
- Task 3 TM: Estimation of Nutrient Loading to Falls Lake. 2013.
- Task 4 TM: Review of Existing Models and Recommendations for Future Studies. 2013.

Work Completed Under "Support of Long-Term Monitoring and Laboratory Services" 2013 Contract with UNRBA:

- TM: Description of the Water Quality Model Framework under the Re-examination Provision of the Falls Lake Rules. 2014.
- TM: Evaluation of the Sensitivity of the Falls Lake Nutrient Response Model. 2014.
- TM: Comparison of Flow Estimation Methods. 2014.
- TM: Water Quality Estimation and Monitoring Optimization. 2014.

In 2010 the Environmental Management Commission (EMC) passed the Falls Lake Nutrient Management Strategy, requiring two stages of nutrient reductions (N.C. Rules Review Commission 2010). The Rules establish a Nutrient Management Strategy for Falls of the Neuse Reservoir aimed at attaining

> "…the classified uses of Falls of the Neuse Reservoir set out in 15A NCAC 02B .0211 from current impaired conditions related to excess nutrient inputs; protect its classified uses as set out in 15A NCAC 02B .0216, including use as a source of water supply for drinking water; and maintain and enhance protections currently implemented by local governments in existing water supply watersheds encompassed by the watershed of Falls of the Neuse Reservoir." (15NCAC 02B .0275)

Stage I of the Nutrient Management Strategy requires "intermediate or currently achievable controls throughout the Falls watershed with the objective of reducing nitrogen and phosphorus loading, and attaining nutrient-related water quality standards in the Lower Falls Reservoir as soon as possible but no later than January 15, 2021, while also improving water quality in the Upper Falls Reservoir…." (15NCAC 02B .0275 (4) (a)). Based on modeling and evaluation by the NC Division of Water Quality (NCDWR), Stage I requires a 20 percent and 40 percent reduction in loading of total nitrogen and total phosphorus, respectively, for point sources and agriculture. For existing development, the rules require that loading be reduced to the baseline year (2006) levels established by NCDWR. Stage I requires local jurisdictions to establish requirements to control nutrient inputs from new development.

Stage II requires that all areas of Falls Lake achieve the nutrient-related water quality standard of 40 µg/l of chlorophyll *a*. Based on NCDWR modeling and evaluation, the additional loading reductions required to achieve this goal are 40 percent and 77 percent for total nitrogen and total phosphorus, respectively, relative to the baseline year. NCDWQ reservoir monitoring data will be used to assess compliance with the goals of the Strategy and determine if additional load reductions to a particular lake segment are needed. As stated in the Rules:

> "Stage II requires implementation of additional controls in the Upper Falls Watershed beginning no later than January 15, 2021 to achieve nutrient-related water quality standards throughout Falls Reservoir by 2041 to the maximum extent technically and economically feasible…." (15NCAC 02B .0275 (4) (b))

Section 5 (f) of the Falls Lake Nutrient Management Strategy recognized the uncertainty associated with the water quality modeling and the Stage II requirements and allows a re-examination of the rules after additional data collection:

> 5(f) Recognizing the uncertainty associated with model-based load reduction targets, to ensure that allowable loads to Falls Reservoir remain appropriate as implementation proceeds, a person may at any time during implementation of the Falls nutrient strategy develop and submit for Commission approval supplemental nutrient response modeling of Falls Reservoir based on additional data collected after a period of implementation. The Commission may consider revisions to the requirements of Stage II based on the results of such modeling as follows:
>
> (i) A person shall obtain Division review and approval of any monitoring study plan and description of the modeling framework to be used prior to commencement of such a study. The study plan and modeling framework shall meet any Division requirements for data quality and model support or design in place at that time. Within 180 days of receipt, the division shall either approve the plan and modeling framework or notify the person seeking to perform the supplemental modeling of changes to the plan and modeling framework required by the Division;
>
> (ii) Supplemental modeling shall include a minimum of three years of lake water quality data unless the person performing the modeling can provide information to the Division demonstrating that a shorter time span is sufficient;
>
> (iii) The Commission may accept modeling products and results that estimate a range of combinations of nitrogen and phosphorus percentage load reductions needed to meet the goal of the Falls nutrient strategy, along with associated allowable loads to Falls Reservoir, from the watersheds of Ellerbe Creek, Eno River, Little River, Flat River, and Knap of Reeds Creek and that otherwise comply with the requirements of this Item. Such modeling may incorporate the results of studies that provide new data on various nutrient sources such as atmospheric deposition, internal loading, and loading from tributaries other than those identified in this Sub-item. The Division shall assure that the supplemental modeling is conducted in accordance with the quality assurance requirements of the Division;
>
> (iv) The Commission shall review Stage II requirements if a party submits supplemental modeling data, products and results acceptable to the Commission for this purpose. Where supplemental modeling is accepted by the Commission, and results indicate allowable loads of nitrogen and phosphorus to Falls Reservoir from the watersheds of Ellerbe Creek, Eno River, Little River, Flat River, and Knap of Reeds Creek that are substantially different than those identified in Item (3), then the Commission may initiate rulemaking to establish those allowable loads as the revised objective of Stage II relative to their associated baseline values.

As established in Section 5 (f) of the Falls Lake Nutrient Management Strategy this UNRBA monitoring plan is being submitted to the Division of Water Resources for their review and approval so that the UNRBA can proceed with their monitoring program. The UNRBA would like to begin their monitoring program at the beginning of July 2014.

This document presents the Upper Neuse River Basin Association's routine monitoring program along with special studies needed to support the UNRBA's three main goals for the monitoring program. This monitoring program assumes that the existing USGS flow gages within the Falls Lake watershed will continue to be supported throughout the four to five year monitoring program. If support is discontinued

for any station(s) in the future, the UNRBA may need to provide funds from its monitoring budget to continue to support flow monitoring (See Figure 1).

The Path Forward Committee of the UNRBA prioritized three monitoring program objectives:

1. Lake response modeling,
2. Support of alternative regulatory options, and
3. Source allocation and estimation of jurisdictional loading.

Objectives 1 and 3 involve routine monitoring at sites on tributaries and in the lake. All three objectives will be supported by targeted special studies aimed at elucidating model parameters, nutrient transformations and nutrient source allocation, and linking water quality to designated uses. This document describes in Section 1.1 the routine monitoring plan for lake response modeling and at jurisdictional boundaries agreed upon by Cardno ENTRIX and the UNRBA. It also identifies special studies to be conducted in support of lake response modeling, identifying source allocation, and facilitating future regulatory options. Not all special studies identified by UNRBA are financially feasible; this document lists only those studies prioritized by the UNRBA with the goal of being completed over the four to five year monitoring program.

In order to streamline DWR's review of the monitoring program Table 1 identifies the different components of the monitoring plan, the UNRBA objectives supported by each, and notes which studies directly support the re-examination process and need approval from DWR. Table 1 also identifies studies that will be used to support the possible development of alternative regulatory options. Descriptions of all the special studies mentioned in Table 1, how the data will be used and their timing are provided in Table 8. Additional information on each special study is provided in Appendix A.

A summary of the UNRBA's monitoring plan for Years 1 through 4 is presented in Table 2. An optional fifth year is included to provide data if abnormal hydrologic conditions are encountered in previous years. As data are collected and analyzed each year, monitoring plans for subsequent years may be refined. The data collected each year will be reviewed and the overall monitoring program re-evaluated to confirm whether adjustments are needed in the frequency and location of data collection or the collection of particular water quality parameters. For example, specific water quality parameters such as chlorophyll *a* collected at the lake loading stations may not be needed for all monitoring years. Any revisions to the monitoring plan will be submitted to the DWR for review and approval prior to the beginning of the next monitoring year.

Tributary sampling locations are shown in Figure 1 and are listed in Tables 3 (Lake Loading sites) and 6 (Jurisdictional Boundary sites) along with the monitoring frequencies, coordinates, and drainage areas of the sampling locations.

Figure 2 identifies the locations in the lake where water quality is monitored by the North Carolina Division of Water Resources (DWR), North Carolina State University's Center for Applied Aquatic Ecology (CAAE), the City of Raleigh, and the City of Durham. Much of the CAAE work is funded by the City of Raleigh.

Detailed information regarding the individual monitoring program components are provided in the following sections. Routine monitoring is described in Section 1.1 and recommended special studies are presented in Section 1.2. The details of each special study can be found in Appendix A.

Table 1 UNRBA Monitoring Program Components

Monitoring Program Component (Section)	Data Use	UNRBA Objectives[1] Supported	For DWR Approval[2]
Routine Monitoring			
Lake Loading at 18 stations (1.1.1)	• To quantify lake loading inputs to Falls Lake EFDC model	1	Y
20 Jurisdictional boundary stations (1.1.3)	• Demonstrate water quality at multiple locations for all UNRBA member organizations	3	N
Special Studies			
Storm event sampling (SS.LR.1)	• Provide additional monitoring data for comparing multiple methods for estimating loads • To assist in selection of best method for estimating loads to Falls Lake	1	Y
Benthic flux and in-lake processes (SS.LR.2)	• To update sediment nutrient flux rates in Falls Lake EFDC model	1	Y
Stream-bank erosion (SS.SA.2)	• Identify nutrient loading associated with instream erosion	3	N
Quarterly diurnal water quality studies (SS.RO.1)	• Support potential development of alternative regulatory approach • Measure simultaneous concentrations of nutrients, chlorophyll a, and physical parameters at multiple lake depths	2	Y
Fish monitoring at seven stations (SS.RO.2)	• Support potential development of alternative regulatory approach • Correlate water quality with fish health	2	N
Drinking water quality and lake monitoring (SS.RO.3)	A. Provide estimate of forms of carbon throughout the lake for Falls Lake EFDC model refinement B. Provide additional data for City of Raleigh regarding fluctuations in TOC concentrations C. Determine whether TOC is generated primarily within Falls Lake or in the watershed	1,2,3	N
Recreational data (SS.RO.4)	• Demonstrate that Falls Lake is supporting recreational uses and correlate use with fluctuations in water quality within Falls Lake	2	N

[1] UNRBA Objectives: 1= Revised Lake response modeling; 2= Support of alternative regulatory options; and 3= Source allocation and estimation of jurisdictional loading.

[2] Y indicates DWR approval is needed for study which will provide data for the re-examination process. N indicates that DWR approval is not needed for the specific study which will be used to support alternative regulatory options.

Table 2 Yearly Schedule for UNRBA Monitoring Program

Monitoring Program Component	Year 1	Year 2	Year 3	Year 4	Year 5 (optional)
Lake Loading at 18 stations	**Twice a month** Ellerbe, Eno, Little, Flat, and Knap of Reeds; **Monthly** all other locations.	**Twice a month** Ellerbe, Eno, Little, Flat, and Knap of Reeds; **Monthly** Little Lick, Lick, Ledge, New Light, and Upper Barton; **Quarterly** all other locations.			
20 jurisdictional boundary stations	**Monthly** monitoring at all locations				
Special Studies	**Year 1**	**Year 2**	**Year 3**	**Year 4**	**Year 5 (optional)**
Storm event sampling	x	X	x	x	x
Benthic flux		X	(alternate year)		
Stream-bank erosion		X			
Quarterly diurnal water quality studies	x	X	x	x	x
Fish monitoring at seven stations	x	X	x	x	x
Drinking water quality and lake monitoring	x	X	x	x	x
Recreational data		X	x	x	x

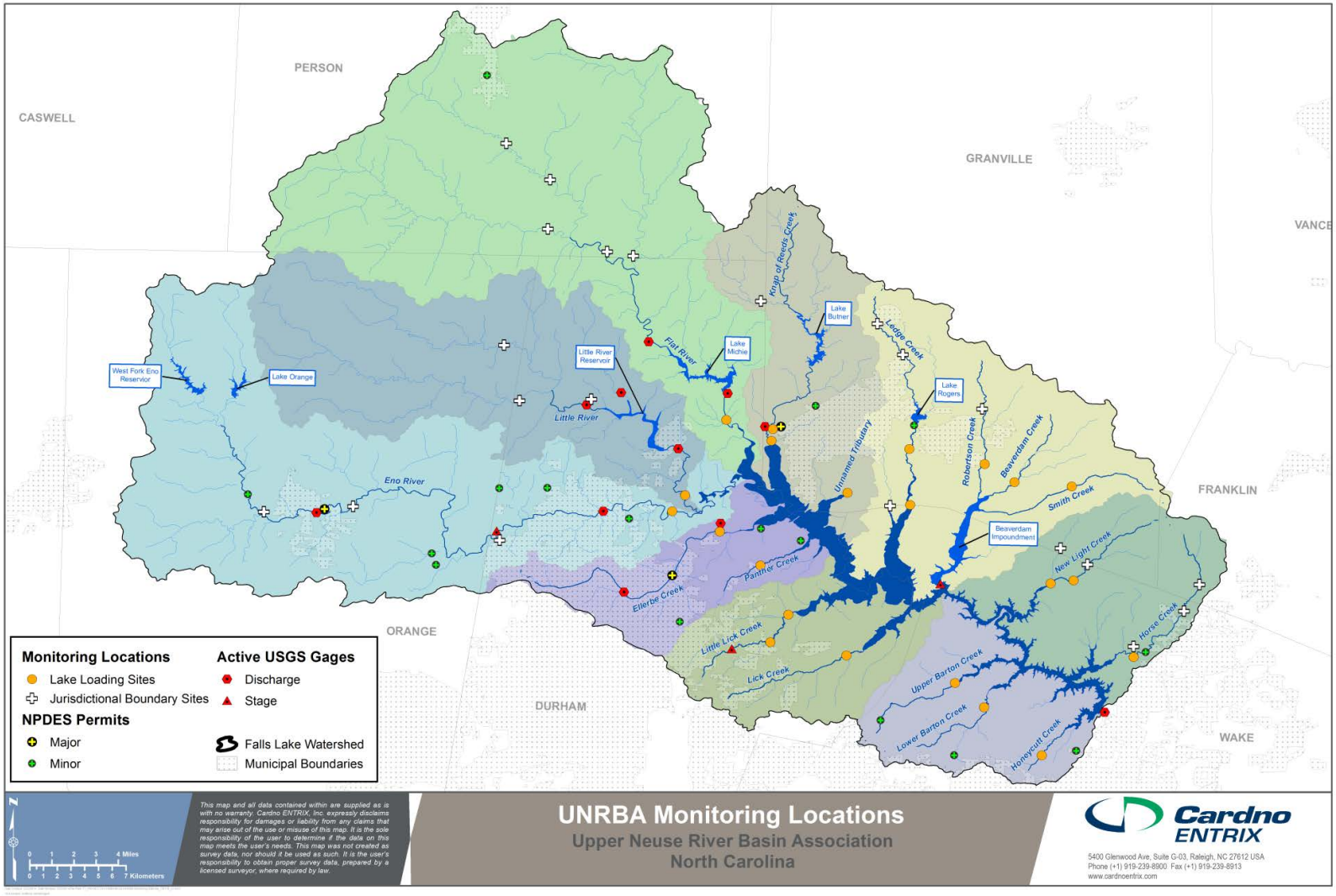

Figure 1 **UNRBA Lake Loading and Jurisdictional Boundary Monitoring locations and existing USGS gages.** Tributaries with 2 Lake Loading Sites displayed will only be monitored at one of the locations shown; the final monitoring site determination will be made based on site visits.

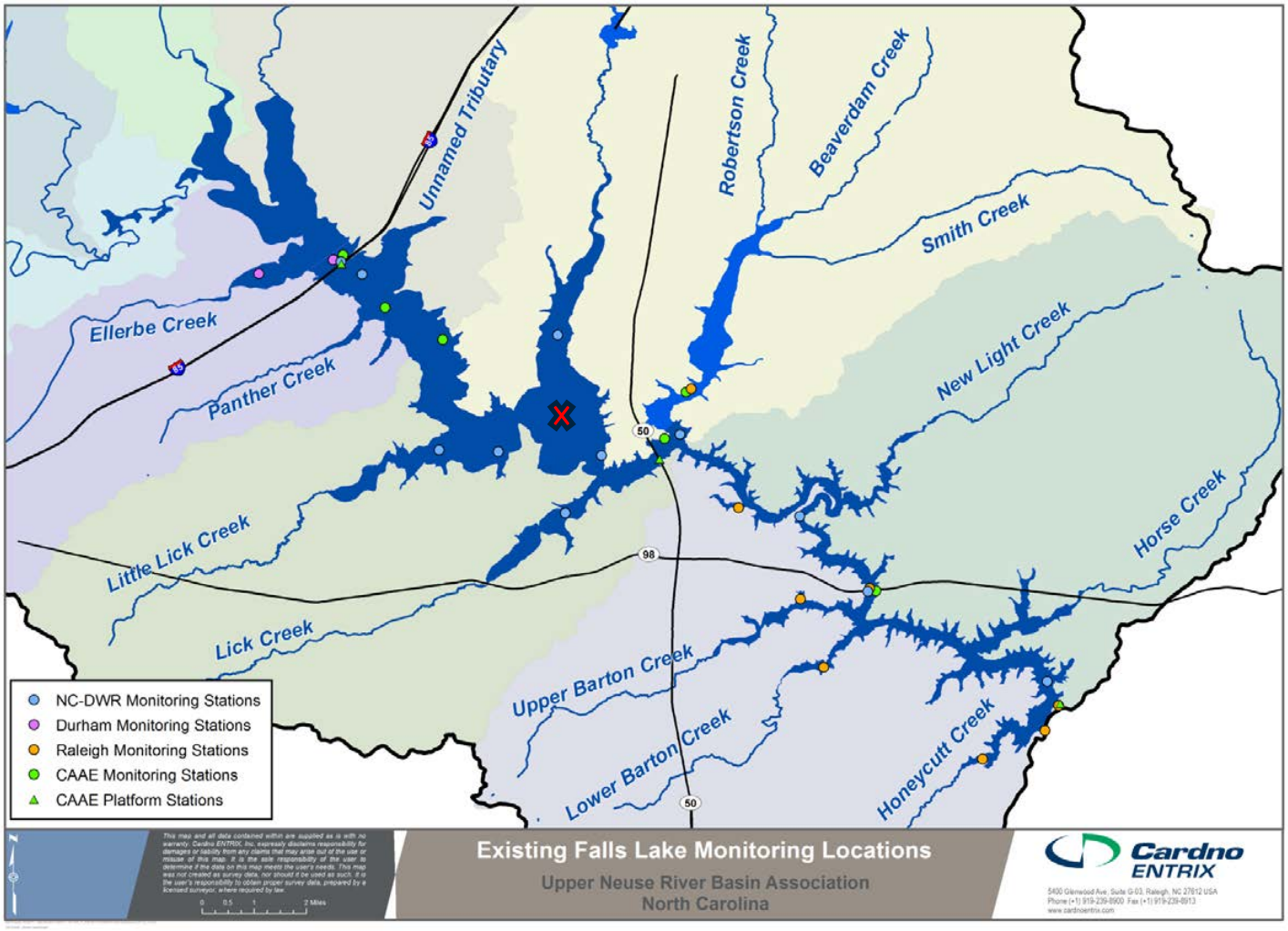

Figure 2 **Falls Lake DWR, CAAE, City of Raleigh, and City of Durham Monitoring Locations. Red X indicates new station UNRBA is requesting that DWR add to their monthly monitoring of Falls Lake.**

1.1 Routine Monitoring

The UNRBA's objectives will be supported by routine monitoring of key water quality parameters (e.g. nutrients, sediment, carbon, and chlorophyll *a*, depending upon location) at designated locations for characterization of loading to the lake, in-lake concentrations, and concentrations at jurisdictional boundaries.

1.1.1 Lake Loading Sites

As described previously by Cardno ENTRIX (2012), the majority of the watershed monitoring data has been collected in the areas that drain to the upper lake. To characterize tributary inputs to support lake modeling, measurements or estimates of flow and water quality are needed at the mouths of each of the tributaries. The current EFDC model setup includes 17 tributary input points. Monitoring data will be collected at 18 tributary input points (the Little River and Eno River will be sampled separately rather than collecting data downstream of their confluence) to facilitate multiple uses of the data including watershed modeling, BMP prioritization, etc.

The tributary sampling will capture various hydrologic regimes. Monitoring at all lake loading sites includes the following parameters: chlorophyll *a*, NH3, NO2/NO3, TKN, Ortho-P, TP, total suspended solids (TSS), total organic carbon (TOC), dissolved organic carbon (DOC), 5-day carbonaceous biochemical demand (CBOD5), specific UV absorbance (SUVA), and field parameters.

The UNRBA monitoring plan balances precision in ability to estimate daily loads with monitoring costs. Sampling will occur twice a month at the five upper lake tributaries which contribute roughly 70-80 percent of the nutrient loading to Falls Lake; it is important to have high confidence in nutrient load estimates in these areas. In years 2 through 4, some tributary loading stations may be reduced to quarterly sampling. However, it is also possible that UNRBA may want to increase sampling frequency at some stations after reviewing initial monitoring data. Such alterations in monitoring frequency will be considered annually by the UNRBA. The current monitoring plan assumes 8 lake loading stations (which together make up less than 10% of the Falls Lake drainage area) could be reduced to quarterly sampling in years 2 through 4.

Table 3 identifies the lake loading stations which will be monitored and sampling frequencies for year 1. Specific tributary sampling locations are identified by nearest road crossing and coordinates. Drainage areas are also provided. These locations are also shown on Figure 1.

Table 3 **Lake Loading Monitoring Locations and Sampling Frequency for the First Monitoring Year.** A total of 18 locations will be monitored.

	Waterbody	Road Crossing	Latitude	Longitude	Drainage Area (mi^2)	Recommended Frequency
LL01	Knap of Reeds Creek	at SGWASA WWTP	36.128000	-78.798530	41.9	Twice per month
LL02	Flat River	at Old Oxford Highway	36.131900	-78.827981	169	Twice per month
LL03	Little River	at Old Oxford Road	36.081667	-78.854722	104	Twice per month
LL04	Eno River	at Old Oxford Highway	36.072642	-78.862700	149	Twice per month
LL05	Ellerbe Creek	at Glenn Road	36.059583	-78.832200	21.9	Twice per month
LL06	Panther Creek	at end of Cooksbury Drive	36.036971	-78.806446	3.24	Monthly
LL07	Little Lick Creek	at Patterson Road	36.004633	-78.787502	13.8	Monthly
LL08	Lick Creek	at Southview Rd south of Hwy 98	35.977936	-78.749565	10.8	Monthly
LL09	Unnamed Tributary	at Northside Road	36.084307	-78.748911	3.43	Monthly
LL10	Ledge Creek	at Highway 15	36.113126	-78.708498	20.3	Monthly
LL11	Robertson Creek	at Brassfield Road	36.102984	-78.659167	12.0	Monthly
LL12	Beaverdam Creek	at Horseshoe Road	36.091260	-78.639854	12.7	Monthly
LL13	Smith Creek	at Lawrence Road	36.088429	-78.602448	6.30	Monthly
LL14	New Light Creek	at Mangum Dairy Road	36.027012	-78.601325	12.3	Monthly
LL15	Horse Creek	at Thompson Mill Road	35.979137	-78.561741	11.9	Monthly
LL16	Upper Barton Creek	at Mt Vernon Church Road	35.959915	-78.678645	8.26	Monthly
LL17	Lower Barton Creek	at State Road 1834 (Norwood Road)	35.943928	-78.659621	10.4	Monthly
LL18	Honeycutt Creek	at Honeycutt Road	35.912558	-78.622060	2.76	Monthly

Parameters for routine monitoring are based on the requirements of the EFDC model along with input from UNRBA member organizations (Table 4). In addition to the standard field parameters and lab analyses for nutrients, TSS, TOC, and chlorophyll *a*, a few additional parameters have been identified for collection and are described below.

Table 4 Water Quality Indicators to be Measured at Lake Loading Sites

Field Measurements	Laboratory Analyses
Water temperature	Total Kjeldahl nitrogen
Air temperature	Soluble Kjeldahl nitrogen
Specific conductance	Nitrate + nitrite
Dissolved Oxygen	Ammonia
pH	Total phosphorus
	Total soluble phosphorus
	Orthophosphate
	Total organic carbon
	Dissolved organic carbon
	Chlorophyll *a*
	Total suspended solids
	Color (or Tannins and Lignin based on Lab input)
	UV absorbance (at 254nm)
	Carbonaceous biochemical oxygen demand (CBOD5)

DOC is a state variable used in the EFDC model along with particulate organic carbon (POC). The POC data will be split into labile and refractory fractions. Monitoring TOC and DOC will allow POC to be calculated by difference. Five-day carbonaceous biochemical oxygen demand (CBOD5) will be used to estimate the partitioning of labile and refractory forms of carbon (Hendrickson et al 2002). This partitioning of carbon will be used in combination with empirical relationships between C:N and C:P ratios as a function of carbon lability in order to further estimate the lability of nutrients (Hendrickson et al 2002).

Color and UV absorbance, which is used with DOC to obtain specific UV absorbance (SUVA), will be used for multiple purposes. Color and SUVA are indicators of the concentration of humic substances in water (Cuthbert and del Giorgio 1992, Weishaar et al. 2003) and can be used to qualitatively identify how much of the carbon pool comes from terrestrial sources versus instream primary production. This can be an important distinction because control of these two sources is achieved by different methods. This information can be used to refine the monitoring plan in future years. Color can be used secondarily to inform the coefficient of background light extinction used in the lake response model. This coefficient affects the availability of light for primary production in the lake. Depending upon the variability of color by tributary or by season, this could be an important factor to consider for calibration of the lake model. Measurement of color and SUVA do not require complicated or time intensive lab work and are relatively inexpensive. All data will be evaluated after each year of collection to verify that the data are meeting the stated objectives. As part of the annual program review, the temporal and spatial resolution of sample collection will be evaluated and changes suggested where appropriate.

1.1.2 Falls Lake Monitoring

Monitoring of Falls Lake provides data for calibration and validation of a revised EFDC model (e.g. concentrations of chlorophyll *a*, nutrients, and carbon) as well as data for informing model parameters (e.g. light extinction coefficient). Ongoing monitoring by DWR, CAAE, and local governments provides data for these efforts (Table 5).

Additional Falls Lake monitoring by the Division of Water Resources (DWR) is requested as part of this monitoring program. A specific proposal that requests that DWR conduct additional lake monitoring will be submitted separately to DWR in conjunction with this monitoring plan. In summary the UNRBA is requesting that DWR add the following water quality analyses to their monthly data collection: total suspended solids (TSS), color, 5-day carbonaceous biochemical oxygen demand (CBOD5), dissolved organic carbon (DOC), and specific UV absorbance (SUVA). The collection of these parameters will help with model calibration. The combination of color, CBOD5, DOC and SUVA will help the UNRBA determine whether carbon sources are primarily derived from inside or outside of the lake. They will also be used to calculate the particulate organic carbon (POC) concentration needed for the model and to estimate what portions of the total are labile and refractory. These data would support future calibration of a revised model, and evaluation of impacts to water quality. The model can be run at the expected ranges of these values to see how the revised model chlorophyll *a* predictions respond to changes in these values. These are not parameters routinely monitored by DWR, but the availability of this data would enhance the re-examination effort and address potential important water supply implications of nutrient levels. If DWR cannot analyze these parameters, their inclusion as a special study of the monitoring program will be considered by the UNRBA and Path Forward Committee. The UNRBA will also request that DWR add one new lake water quality station in the center of the lake downstream of the mouth of Ledge Creek (coordinates are approximately 36.025,-78.716). The location of this proposed new station is shown as a red X on Figure 2. The addition of this station to the DWR's Falls lake monitoring program would provide data for the model in an area of the lake which is considered underrepresented by current monitoring. If DWR is willing to monitor this additional lake station the UNRBA, in conjunction with DWR, will evaluate the data from this new site following 18 months of data collection to determine whether monitoring should continue over the life of the monitoring program or be discontinued. This evaluation will be done to confirm that the data collected at the new site provides information helpful to the UNRBA's objectives of revised Lake response modeling and Support of alternative regulatory options.

If the DWR cannot add this station, its inclusion as a special study in one or more subsequent years will be considered by the Path Forward Committee. Based on DWR's response to the additional proposed Falls Lake monitoring plan it may be necessary to modify this monitoring plan. At previous meetings with DWR, there was general indication that, if possible, the Division would be willing to provide some additional monitoring coverage to enhance the UNRBA's program.

The Center for Applied Aquatic Ecology (CAAE) monitors DO, temperature, pH, and specific conductivity every three hours at multiple depths at three platforms located at I-85, Creedmoor Road, and at Raleigh's intake. Additional parameters are monitored monthly and up to bi-weekly during the summer at these stations. The CAAE data will be used to inform model calibration and can be paired with diurnal water quality sampling as a recommended special study (Appendix A). This study will provide the UNRBA with data needed to support development of site specific water quality criteria or a sub-classification use attainability analysis, and correlates chlorophyll *a* concentrations with conditions that influence aquatic health. The study will also provide additional calibration data for the EFDC model.

Table 5 Current Lake Sampling by DWR, Cities of Durham and Raleigh, and CAAE.
Frequencies are provided in parentheses: M-monthly, W-weekly..

Samples	DWR	City of Durham	City of Raleigh	CAAE
TOC	Photic Zone Composite (M)	Surface and/or Photic Zone Composite[1] (W)	Surface (M)	Monthly with seasonal increase in frequency at the three platforms (I-85, Hwy 50, and Raleigh Intake), variable frequency elsewhere[2]
Chlorophyll *a*	Photic Zone Composite (M)	Surface and/or Photic Zone Composite[1] (W)	Surface (M)	**Hwy 85, Hwy 50, and Raleigh Intake** 1-2 meters, 2x/month **Variable sampling frequency at other locations**
TN	Photic Zone Composite (M)	Surface and/or Photic Zone Composite[1] (W)	Surface (M)	Monthly with seasonal increase in frequency at the three platforms (I-85, Hwy 50, and Raleigh Intake), variable frequency elsewhere[2]
TKN	Photic Zone Composite (M)	Surface and/or Photic Zone Composite[1] (W)	Surface (M)	Monthly with seasonal increase in frequency at the three platforms (I-85, Hwy 50, and Raleigh Intake), variable frequency elsewhere[2]
NO2 + NO3	Photic Zone Composite (M)	Surface and/or Photic Zone Composite[1] (W)	Surface (M)	Monthly with seasonal increase in frequency at the three platforms (I-85, Hwy 50, and Raleigh Intake), variable frequency elsewhere[2]
NH3	Photic Zone Composite (M)	Surface and/or Photic Zone Composite[1] (W)	-	Variable
TP	Photic Zone Composite (M)	Surface and/or Photic Zone Composite[1] (W)	Surface (M)	Monthly with seasonal increase in frequency at the three platforms (I-85, Hwy 50, and Raleigh Intake), variable frequency elsewhere[2]
Orthophosphorus	-	Surface and/or Photic Zone Composite[1] (W)	-	-
Turbidity	Photic Zone Composite (M)	-	Surface (M)	-

Samples	DWR	City of Durham	City of Raleigh	CAAE
TSS	-	-	-	Monthly with seasonal increase in frequency at the three platforms (I-85, Hwy 50, and Raleigh Intake), variable frequency elsewhere[2]
pH	Depth Stratified (M)	Surface (W)	Surface (M)	Platforms[3]
Conductivity	Depth Stratified (M)	Surface (W)	Surface (M)	Platforms[3]
Dissolved oxygen	Depth Stratified (M)	Surface (W)	Surface (M)	Platforms[3]
Temperature	Depth Stratified (M)	Surface (W)	Surface (M)	Platforms[3]

[1] Durham has two stations: one has data only for surface samples, the other has data for surface and photic zone composite samples.

[2] Data are available for a number of CAAE sites which are either no longer sampled, are sampled only in summer months or have variable sampling frequency for these parameters.

[3] These data are collected from *in situ* monitoring platforms at multiple depths every three hours.

1.1.3 Jurisdictional Boundary Sites

Establishment of water quality monitoring stations at jurisdictional boundaries and key loading points such as the outlets of major tributaries within a jurisdiction can be used to 1) provide water quality data from multiple areas within all member jurisdictions, 2) prioritize BMP implementation in areas with the highest nutrient loading, 3) calibrate watershed models and, potentially, 4) assess changes in loading over time.

Twenty unique stations have been selected to characterize water quality at jurisdictional boundaries within the Falls Lake watershed (excluding those covered under the lake loading stations) based on input from the UNRBA Path Forward Committee (Figure 1, Table 5). These 20 stations will be monitored every month for the first year. Cost savings may be realized in subsequent years if sampling frequency can be reduced to every-other month or quarterly at some stations. Based on Path Forward Committee recommendations, we assume that the monthly sampling frequency will continue in each year. Monitoring frequency will be revisited with the UNRBA on at least an annual basis.

The water quality measurements at jurisdictional boundary locations will initially include the following parameters: ammonia (NH3), nitrate plus nitrite (NO2/NO3), total Kjeldahl nitrogen (TKN), total phosphorus (TP), total suspended solids (TSS), total organic carbon (TOC), and field parameters (temperature, dissolved oxygen, pH, and conductivity). These parameters are listed in Table 7.

Table 6 Jurisdictional Boundary Monitoring Locations. All stations will be sampled monthly.

	Waterbody	Road Crossing	Boundary	Latitude	Longitude	Drainage Area (mi^2)	Monitoring Frequency
JB01	Eno River	at Dimmocks Mill Road	upstream of Hillsborough	36.070127	-79.129530	60.5	Monthly
JB02	Eno River	at Hwy 70 and Riverside Drive	downstream of Hillsborough	36.075417	-79.071636	73.2	Monthly
JB03	Eno River	at Cole Mill Road	downstream of Orange County	36.059290	-78.978042	121	Monthly
JB04	North Fork Little River	at New Sharon Church Road	between Orange and Durham Counties	36.180164	-78.975432	21.9	Monthly
JB05	South Fork Little River	at Guess Road (Hwy 157)	between Orange and Durham Counties	36.145465	-78.962187	37.4	Monthly
JB06	Little River	at Johnson Mill Road	upstream of City of Durham	36.141643	-78.919265	78.3	Monthly
JB07	North Flat River	at Highway 57	downstream of Roxboro	36.310638	-78.969420	15.8	Monthly
JB08	North Flat River	at Helena-Moriah Road	Person Co. before confluence with South Flat	36.288983	-78.942891	32.8	Monthly
JB09	South Flat River	at Highway 57	Person Co. before confluence with North Flat River	36.256842	-78.944337	54.4	Monthly
JB10	Flat River	at Moores Mill Road	downstream of Person county	36.241864	-78.905769	102	Monthly
JB11	Deep Creek	at Smith Road	downstream of Person County	36.240278	-78.888885	32.1	Monthly
JB12	Camp Creek	at Camp Butner	between Durham and Granville Counties	36.209510	-78.805304	4.99	Monthly
JB13	Little Ledge Creek	at Old Weaver Trail	downstream of Granville	36.075904	-78.720953	3.74	Monthly
JB14	Ledge Creek	at Old Route 75	downstream of Stem	36.194856	-78.729220	1.79	Monthly
JB15	Ledge Creek	at W Lyon Station Road	upstream of Butner	36.176079	-78.714097	3.49	Monthly
JB16	Robertson Creek	at Sam Moss Hayes Road	upstream of Creedmoor	36.139193	-78.660785	4.43	Monthly
JB17	Buckhorn Creek	at Buckhorn Lane	between Granville and Wake Counties	36.048080	-78.609717	1.21	Monthly
JB18	New Light Creek	at Bold Run Hill Road	between Granville and Wake Counties	36.037485	-78.592078	9.90	Monthly
JB19	Horse Creek	at Holden Road	between Franklin and Wake Counties	36.024301	-78.518988	4.78	Monthly
JB20	Horse Creek	at Purnell Road	upstream of Wake Forest	36.007058	-78.529087	7.11	Monthly

Table 7 Water Quality Parameters to be Measured at Jurisdictional Boundary Sampling Locations

Field Measurements	Laboratory Analyses
Water temperature	Total Kjeldahl nitrogen
Air temperature	Nitrate + nitrite
Specific conductance	Ammonia
Dissolved oxygen	Total phosphorus
pH	Total organic carbon
	Total suspended solids

1.2 Special Studies Component of the Monitoring Program

In addition to routine monitoring as described in Section 1.1 of this Monitoring Plan, several short-term studies will provide critical data needed to support each of the UNRBA's monitoring objectives. Over the past several years, UNRBA members and Cardno ENTRIX have identified many special studies that would inform the program's monitoring objectives; however, the total cost of these studies exceeds the UNRBA budget. This section presents the special studies which have been ranked highly jointly by Cardno ENTRIX and the UNRBA Path Forward Committee and are selected for inclusion in the 4-5 year monitoring program.

Recommended special studies along with their timing are presented in Table 8 and are grouped according to the three UNRBA monitoring objectives: lake response modeling, jurisdictional loading and source allocation, and support for regulatory options. Not all recommended special studies occur every year, and several studies will only occur in one or two years. The Study ID number corresponds to further discussion of the study in Appendix A and follows the format SS.XX.#, where SS stands for "Special Study", XX refers to the monitoring objective the special study meets. The monitoring objectives are "LR" for "Lake Response Modeling", "SA" for "Source Allocation" or "RO" for "Regulatory Options". The final number distinguishes among special studies within a given category.

Table 8 Special Studies and Data Use, Importance, and Timing of Study Implementation

Study ID	Special Study Description	How information will be used by UNRBA and why it is important to the UNRBA	Estimated Duration
Lake Response Modeling (Loading Estimation)			
SS.LR.1	Storm event sampling and comparison of loading methods	Determine which method (various LOADEST options or WQ statistical model) most accurately calculates nutrient loads to Falls Lake. The TN and TP load estimate doubles depending on the method used as shown in the Model Sensitivity TM. Estimating lake loads based on the most accurate method will result in substantially more accurate model predictions and increased confidence in resulting Stage II targets.	1-2 storms per year, each at one site. Sites will vary for each storm.
SS.LR.2	Obtain additional internal loading from lake sediments	Improve accuracy and calibration of EFDC model. If EPA cannot collect this data, the data collected by DWR will be used to revise model setup, applying the higher nutrient flux measurements in upper lake areas. Although DWR collected data at two sites and obtained different flux rates at each, the current model uses a single value for the entire lake.	UNRBA will seek DWR cooperation to petition EPA to conduct these surveys for Falls Lake.
Source Allocation: Determining Loading from Different Watershed Sources			
SS.SA.1	Tracking BMP Implementation, Inspections and Repairs	The following information should be collected: description of each BMP, geographic position, parcel square footage, square footage by land use draining to the BMP, and BMP inspections and maintenance performed. The Nutrient Scientific Advisory Board (NSAB) is currently establishing guidance regarding data collection efforts for BMPs that will be needed to calculate credits. To continue receiving nutrient loading credits from BMPs, local governments should inspect and repair BMPs on an annual basis.	This information should be tracked annually by member jurisdictions.
SS.SA.2	Measure cross sections and sediment concentrations at five locations previously monitored by USGS; estimate sediment and nutrient loading associated with stream bank erosion	Determine how much of the nutrient loading to the lake could be associated with stream bank erosion; used to support development of nutrient reduction credits assigned to stream restoration activities. Provides members the ability to prioritize implementation practices and reduce compliance costs.	Conduct in year 2. UNRBA will discuss with USGS to determine if they are interested in revisiting these studies.

Study ID	Special Study Description	How information will be used by UNRBA and why it is important to the UNRBA	Estimated Duration
Support of Regulatory Options - Linkage of Water Quality with Designated Uses			
SS.RO.1	Water quality studies at three Center for Applied Aquatic Ecology (CAAE) diurnal stations (I-85, Highway 50, and Raleigh Intake) during high-chlorophyll periods.	Supports regulatory options and structural equation/ Bayesian modeling, and EFDC model calibration. Provides data needed to support development of site specific water quality criteria or a sub-classification use attainability analysis. Correlates chlorophyll *a*, nutrient, DO and pH concentrations with conditions that influence aquatic health.	Years 1, 2, 3, 4
SS.RO.2	Fish monitoring by WRC at DWR Lake monitoring stations (or at the three CAAE locations)	Support regulatory options and structural equation/ Bayesian modeling. Correlates fish population, size and length with water quality conditions in the three main segments of the lake.	Years 1, 2, 3, 4
SS.RO.3	Coordinate with the City of Raleigh to conduct paired water quality sampling (nutrients, chlorophyll *a*, TOC, DOC, SUVA, and color) at intake to correlate with finished water quality testing performed by Underwriters Laboratories (UL) (taste and odor and DBPs)	Support regulatory options and structural equation/Bayesian modeling. Provides data to identify how water quality at the intake is linked with disinfection byproduct formation and taste and odor issues in the finished water.	Years 1, 2, 3, 4
SS.RO.4	Recreational surveys and count models that link visitation with water quality parameters	Support regulatory options and structural equation/Bayesian modeling. Correlates lake water quality with recreational uses. These data are needed for development of a site specific criterion or a sub-classification use attainability analysis.	Years 2, 3, 4, and 5 if needed

2 List of References

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Cardno ENTRIX. 2013b. Task 3: Estimation of Nutrient Loading to Falls Lake. Support of Long Term Planning and Regulatory Nutrient Activities in the Falls Lake Watershed. Prepared for the Upper Neuse River Basin Association.

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Final UNRBA Monitoring Plan

APPENDIX A

DESCRIPTION OF SPECIAL STUDIES

Appendix A Final UNRBA Monitoring Plan
Description of Special Studies

Appendix A

A.1 Studies to Support Revised Lake Response Modeling

The existing Falls Lake EFDC lake response model was developed based on lake and watershed data collected from 2005 to 2007. In addition to the routine monitoring described in the main text of this document to better characterize tributary loading of nutrients, carbon, and chlorophyll *a*, several potential special studies have been identified which could reduce the reliance on assumptions for model development and influence the model response.

The following special studies related to Lake Response Modeling are deemed high priority and may be conducted within the currently projected UNRBA monitoring budget. Future changes to the budget or monitoring priorities established by the UNRBA may influence whether these special studies can be completed.

SS.LR.1: Storm Event Sampling

In a recent TM describing the sensitivity of the EFDC lake response model, Cardno ENTRIX demonstrates several methods for estimating nutrient loads to the lake based on flow and water quality data. The loads resulting from each method were highly variable and a determination of which method was most accurate could not be made based on the data available. Conducting storm event sampling where flow and water quality samples are collected frequently over the course of a storm will provide the data needed to determine which of the methods is most accurate in determining loading to the lake. The following water quality parameters should be included: turbidity, NH3, NO2/NO3, TKN, Ortho-P, total P, TSS, TOC, field parameters, and sediment partitioning. Sampling frequency will vary based on the intensity and duration of the storm. These studies will be conducted initially where an existing 15-minute USGS flow gage is present. One to two sites will sampled, each for a single storm event, in each year of the monitoring program.

SS.LR.2: Internal Lake Loading

The assessment of nutrient loading to the lake should account for internal loading due to releases from lake sediment. Benthic flux rates should be measured for ammonia, nitrate plus nitrite, phosphate, and sediment oxygen demand (SOD). There are a small number of existing measurements of benthic flux in Falls Lake that were conducted in support of the EFDC lake response modeling, and these results suggest that different rates may apply to different locations within the lake. However, the existing Falls Lake EFDC model assumed a single rate for each parameter across the lake which was adjusted as a calibration factor. In addition, the existing measurements were conducted in the spring when hypoxic conditions at the sediment-water interface were likely not present. Low dissolved oxygen conditions stimulate the release of phosphorus from lake sediments, so the existing monitoring may not have characterized the actual variability in this nutrient loading source.

A better understanding of the spatial variability in these lake processes would improve model calibration and provide the data needed to simulate these processes spatially rather than assuming that one set of factors applies in all areas of the lake. Future model updates could account for the observed spatial variation at additional stations, and sampling events would provide greater characterization of the spatial and temporal variability across the lake as whole. Additional monitoring for benthic flux should include both temporal (seasonal) and spatial variation. These

measurements will provide additional information on the spatial variability of these rates, but as with any monitoring plan additional data collection does not eliminate all uncertainty.

Benthic nutrient flux and sediment oxygen demand are measured *in situ* using sealed chambers. Samples are extracted from the water above the sediments and changes in nutrient concentration are used to calculate flux (mass per time). Measurements are typically taken in triplicate at each site. Site locations will be selected to assess longitudinal changes in nutrient flux from the upstream end of the lake to the dam.

Because the sediment oxygen demand studies require the presence of dissolved oxygen at the sediment-water interface to measure rates of change in this parameter, these benthic studies will not be conducted under anoxic conditions when phosphorus flux is typically greatest.

The UNRBA will petition US-EPA Region 4 to conduct these studies. If EPA does not conduct these studies, then the model may be modified to use the higher flux rates obtained by DWR at I-85 to represent conditions in the lake upstream of Creedmoor Road. The lower flux rates will be used to represent conditions in the lake downstream of Creedmoor Road. Alternatively, the two spatial measurements could be used to define a linear change in benthic flux rates defined for several modeling segments. Both approaches could be tested during preliminary model revisions and the sensitivity of the model to these parameters could be assessed.

A.2 Source Allocation and Estimation of Jurisdictional Loading and Nutrient Transport within the Falls Lake Watershed

In order to achieve compliance with chlorophyll *a* water quality standards throughout the Lake, the State has determined that nutrient loading to the lake from the upper five tributaries should be reduced by 40 percent for nitrogen and 77 percent for phosphorus. The Falls Lake Nutrient Management Strategy rules identify the parties (municipalities, counties, agriculture, and state and federal entities) responsible for implementing the nutrient reductions, which are to be achieved by requiring stormwater controls and implementation of best management practices (BMPs) for new and existing development, point source discharges, and agricultural non-point sources. Due to the requirements specified in the Falls Lake Nutrient Management Strategy (.0275 5(b)(i)), nutrient loading to Falls Lake Reservoir must be evaluated and reported to the EMC every five years, beginning in 2016.

Current evaluations of the watershed model indicate that there is a high degree of uncertainty associated with the watershed loads predicted by the Falls Lake watershed loading (WARMF) model. Issues and uncertainties associated with the model have been described by Cardno ENTRIX (2013b).

Targeted monitoring within the watershed will reduce uncertainties associated with specific loading sources and jurisdictional allocations. This monitoring can be supplemented by the statistical models developed by Cardno ENTRIX in the Water Quality Estimation and Optimization TM (Cardno ENTRIX April 2014). The following studies would provide data that can be used to refine the watershed loading estimates to Falls Lake, validate and refine the statistical models, and increase the accuracy of jurisdictional load allocation. Future changes to the budget or monitoring priorities established by the UNRBA may influence whether these special studies can be completed as described.

SS.SA.1: Tracking BMP implementation, inspections, and repairs

Local governments in the Falls Lake watershed are required to track BMP implementation and estimate resulting nutrient load reductions. Local governments should begin collecting data to support this requirement and provide the data needed for credit accounting tools such as the Jordan/Falls Lake Stormwater Nutrient Loading Accounting Tool (NCSU-BAE and NCDENR 2011). The following information should be collected: description of each BMP, geographic position, parcel square footage, square footage by land use draining to the BMP, and BMP inspections and maintenance performed. The Nutrient Scientific Advisory Board (NSAB) is currently establishing

guidance regarding data collection efforts for BMPs that will be needed to calculate credits. To continue receiving nutrient loading credits from BMPs, local governments should inspect and repair BMPs on an annual basis. Cardno ENTRIX suggests that each UNRBA member document these efforts in an electronic database or spreadsheet. These efforts will be covered by individual local governments. The local governments should treat this as a high priority effort.

SS.SA.2: Streambank erosion and nutrient loading

Little is known regarding the contribution of streambank erosion to nutrient loading in the Falls Lake watershed. Monitoring to measure the relative importance of this source is recommended. There are several locations in the watershed where USGS obtained stream channel cross section measurements. Revisiting these sites and measuring the cross sections will provide an estimate of the mass of sediment lost. Collecting stream bank and stream bed sediment data for analysis of nutrient and carbon content will provide a corresponding estimate of loading for these parameters. Another option (more resource intensive) is to develop Bank-Stability and Toe-Erosion Models (BSTEM) that rely on additional field data and the use of bank erosion modeling to estimate sediment loading under baseline and management scenarios. Given the other priorities associated with this monitoring program, Cardno ENTRIX recommends the simpler option that relies on cross section and sediment nutrient concentration data. This is a high priority study because its results will provide the UNRBA with information needed to prioritize BMPs on upland areas versus stream bank restoration projects.

A.3 Support of Regulatory Options and Linkage of Water Quality to Designated Uses

Falls Lake is listed as impaired for chlorophyll *a* based on the water quality criteria of 40 µg/L. The framework for re-examining the Falls Lake Nutrient Management Strategy relies on a linkage between water quality and designated uses: wildlife enhancement and aquatic life, recreation, drinking water supply, and flood storage. To date, little data has been collected in Falls Lake to support this linkage, and even DWR staff have stated that "based on what DWR staff has read in files from the 1970s, Water Resources Research Institute (WRRI) did not have a specific designated use that they were trying to protect by utilizing the 40 µg/L chlorophyll *a* criteria" (August 29, 2005 Falls of the Neuse and High Rock Lakes Combined Technical Advisory Committee meeting). Several studies are needed to provide a better linkage between water quality and designated uses, particularly with respect to the chlorophyll *a* standard.

The following special studies related to supporting regulatory options are deemed high priority and may be conducted within the currently projected UNRBA monitoring budget. Future changes to the budget or monitoring priorities established by the UNRBA may influence whether these special studies can be completed as described.

SS.RO.1: Falls Lake diurnal pH and DO monitoring with water quality sampling

The purpose of this study is to obtain additional data throughout the water column to link the aquatic life use support category with concentrations of chlorophyll *a*, nutrients, and related fluctuations in dissolved oxygen (DO) and pH. An over-abundance of algae may cause diurnal variations in DO concentrations and pH levels as the processes of photosynthesis and respiration occur. Die-off and decay of algae also result in the consumption of DO.

North Carolina State University's Center for Applied Aquatic Ecology (CAAE) collects field data at three hour increments at three locations in Falls Lake with at least monthly water quality sampling. Diurnal sampling of DO, pH, and temperature at these three CAAE platform locations (at multiple depths) in the lake will provide an indication of whether aquatic organisms are likely experiencing stress due to elevated levels of algae in the water column. To supplement the CAAE field data collection, water quality samples should be collected during 2-3 high algal growth periods

and one lower algal growth period to link chlorophyll *a* and nutrient concentrations with fluctuations in DO and pH and document conditions which can impact support of the aquatic life use. Data will be collected once per day for a 4-day period as a photic zone composite and at three discrete depths. Sampling depths should be co-located at the depths monitored by the automated platform and be approximately one meter from the surface, one meter from the bottom (or at the deepest CAAE platform sampling depth), and near the middle of the water column. Monitoring will include the following parameters: chlorophyll *a*, NH3, NO2/NO3, TKN, Ortho-P, total P, TSS, color, SUVA, TOC, and DOC. Algal unit density (units/ml) and biovolume (mm^3/m^3) will also be obtained for the following three groups of algae: diatoms, green algae, and cyanobacteria.

The data from this study can be used to demonstrate support of the aquatic life use and for development of an alternative chlorophyll *a* criterion for sections of Falls Lake. This data will also be used to help calibrate the EFDC model and provide insight on day to day variability in nutrient and chlorophyll *a* concentrations. If day-to-day variability is found to be high, the time interval between water quality samples may be decreased for subsequent monitoring events. This is a high priority study.

SS.RO.2: Fish monitoring with water quality sampling

The NC Wildlife Resources Commission (WRC) conducts fish monitoring in Falls Lake once per year for either largemouth bass or black crappie. The majority of the fish monitoring occurs in the Lower Lake downstream of Highway 50 (94 percent of current surveys focus on the Lower Lake). Fish monitoring in the Upper Lake would provide information on the biological health in this part of the system. This effort would involve coordinating with the WRC so that the fish sampling occurs within a few days of the monthly lake sampling conducted by DWR. This will provide an indication of how water quality affects fish utilization of the lake. Coordination with the WRC will be required to develop this sampling plan. This is a high priority study.

SS.RO.3: Drinking Water Supply and Water Quality Monitoring

The City of Raleigh currently collects data on taste and odor, disinfection by-products, and other parameters associated with the quality of the raw water supply at several places below Highway 50 (Figure 2). Cardno ENTRIX recommends water quality sampling of raw water for additional parameters including nutrients, chlorophyll *a,* TOC, DOC, SUVA, and color to link water quality at the intake with quality measures for finished water.

Appendix A Final UNRBA Monitoring Plan
Description of Special Studies

SS.RO.4: Recreational Data and Water Quality Sampling

Weekly recreational count data are available from the State Park System for the period 2000 to 2011. Starting in 2012, daily data are available. User perception surveys conducted to supplement the State Park System counts will be implemented online to assess how water quality conditions (clarity, aesthetics, odor, etc.) impact the quality of the recreational experience and dictate choices regarding where and when people choose to recreate. These online surveys will provide a linkage between water quality and attainment of the recreational designated uses for the reservoir. Surveys should target a mix of recreational uses including fishing, swimming, and boating to determine if water quality affects these uses in different ways.

The following recreational survey and count model development is recommended:

- Year 2: analyze count data from State Parks and develop count model to assess trends with weather, lake water quality, etc. Present results as a power point presentation to the UNRBA and develop a user-perception survey if needed (this will depend on the trends and strengths of the count model)
- Year 3: implement the user perception survey via internet to 1000 participants during the summer months. Update the count model and draft a report that summarizes the count model and the results of the user perception survey. Determine if additional surveys are needed in Year 4.
- Year 4 as needed: implement the user perception survey via internet to 1000 participants during the summer months. Update the count model and update the report that summarizes the count model and the results of the user perception survey. Determine if additional surveys are needed in Year 5.
- Year 5 if needed: implement the user perception survey via internet to 1000 participants during the summer months. Update the count model and report that summarizes the count model and the results of the user perception survey.

Appendix A Final UNRBA Monitoring Plan
Description of Special Studies

Table A-1. Summary of Special Studies.

Study ID	Priority	Study	Year 1	Year 2	Year 3	Year 4	Year 5 (Optional)
SS.LR.1	High	Storm event sampling	2 events	1 event	2 events	2 events	2 events
SS.LR.2	High	Internal lake loading. Petition EPA to conduct these studies.	Work with DWR to petition EPA to conduct studies	Schedule studies	Schedule studies – Alternate Year		
SS.SA.1	High	Tracking BMP Implementation, Inspections, and Repairs	x	x	x	x	x
SS.SA.2	High	Measure cross sections and sediment nutrient concentrations at five previously monitored locations; estimate sediment and nutrient loading associated with stream bank erosion		x			
SS.RO.1	High	Quarterly water quality studies at three CAAE diurnal stations	x	x	x	x	x
SS.RO.2	High	Fish monitoring at seven stations	x	x	x	x	x
SS.RO.3	High	Drinking water quality and lake water quality monitoring	x	x	x	x	x
SS.RO.4	High	Recreational data		x	x	x	x

Final UNRBA Monitoring Plan

APPENDIX B

DWR APPROVAL OF UNRBA MONITORING PLAN

Appendix B

B.1 DWR Approval of UNRBA Monitoring Plan

North Carolina Department of Environment and Natural Resources

Pat McCrory
Governor

John E. Skvarla, III
Secretary

July 16, 2014

Dear Mr. Westall:

DWR approves UNRBA's Monitoring Plan under the Falls Lake Rules 15A NCAC 02B .0275 (5) (f). This approval applies only to the parts of the plan that support the goal of "develop and submit for Commission approval supplemental nutrient response modeling of Falls Reservoir" as per the Falls Lake Rules. This approval is contingent on the submittal and DWR approval of any future changes to the monitoring plan.

DWR approval of UNRBA's Monitoring QAPP must be obtained before monitoring begins, as provided for in the Falls Lake Rules. If you have questions, please contact Kathy Stecker of DWR's Modeling and Assessment Branch. Thank you and UNRBA for your commitment to improving water quality in Falls Lake.

Sincerely,

T. C. Fransen

Tom Fransen, Chief
Planning Section
Division of Water Resources

cc: Tom Reeder
Dianne Reid
Kathy Stecker
Steve Kroeger

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Appendix 2
to the UNRBA Monitoring Program QAPP

NC Wastewater/Groundwater Laboratory Certification Approved Procedures

Table of Contents

NORTH CAROLINA WASTEWATER/GROUNDWATER LABORATORY CERTIFICATION APPROVED PROCEDURE FOR THE ANALYSIS OF DISSOLVED OXYGEN (DO)

This document provides an approved procedure for the analysis of DO per 15A NCAC 2H .0805 (a) (6) (F) and (g) (3). The procedures in this document, in addition to all requirements of the EPA approved method found in 40 CFR Part 136.3, must be met.

HOLDING TIME:

- Samples must be analyzed within 15 minutes of collection (40 CFR Part 136 Table II); however, *in situ* or immediate analysis is recommended due to the unstable nature of dissolved oxygen in samples.

GENERAL INFORMATION:

- Types of probes:

    a. Dissolved Oxygen Membrane Electrode
    b. Luminescence Dissolved Oxygen (LDO) Sensor

- Movement of water across the membrane (for membrane electrode technologies) is important to good readings. Some probes come with stirrers for this purpose. Measurements should be taken while the stirrer is in use or by swirling the DO probe in the sample flow.

- Follow the manufacturer's instructions for probe storage.

METER CALIBRATION:

- Instruments are to be calibrated according to the manufacturer's calibration procedure prior to analysis of samples each day compliance monitoring is performed.

- The laboratory must use moist air for the air calibration. This is accomplished by calibrating the electrode in an environment with a high relative humidity. Using dry air for the calibration can result in errant readings.

- The laboratory must document each time that a calibration is performed. Calibration documentation must include the following, where applicable to the instrument used and the type of calibration performed: elevation, temperature, barometric pressure (in mmHg), salinity, slope, or %efficiency. Simply recording a final reading (in mg/L) for instruments that auto calibrate (e.g., LDO sensors and Membrane Electrodes that AUTOCAL) is also acceptable.

- For LDO sensors that cannot be calibrated, the calibration must be verified each day of use. This can be performed by back calculating the theoretical DO for the current air calibration conditions (e.g., temperature, elevation, barometric pressure, etc.). The calculated DO value must verify the meter reading within ±0.5 mg/L. Refer to the *Dissolved Oxygen Meter Calibration Verification* handout at the end of this document. If the meter verification does not read within ±0.5 mg/L of the theoretical DO, corrective action must be taken.

- When performing analyses away from the certified laboratory's primary location, a post analysis calibration verification must be analyzed at the end of the run. It is recommended that a mid-day calibration verification be performed when samples are analyzed over an extended period of time. The calculated DO value must verify the meter reading within ±0.5 mg/L. If the meter verification does not read within ±0.5 mg/L of the theoretical DO, corrective action must be taken.

DOCUMENTATION:

The following must be documented in indelible ink whenever sample analysis is performed.

1. Date and time of sample collection.

Rev. 04/2013

2. Date and time of sample analysis to verify the 15 minute holding time is met. Alternatively, one time may be documented for collection and analysis with the notation that samples are measured *in situ* or immediately at the sample site.
3. Sample site including facility name and location, ID, etc.
4. Collector's/analyst's name or initials.
5. Meter calibration and meter calibration time(s).
6. True value and value obtained for the post analysis calibration verification(s), where applicable.
7. All data must be reported in mg/L.
8. Instrument identification.
9. Parameter analyzed.
10. Data qualifier(s), when applicable.
11. Equipment maintenance (recommended).

Refer to *Quality Assurance Policies for Field Laboratories* (at http://portal.ncdenr.org/web/wq/lab/cert/field/policy) for additional quality assurance and quality control requirements.

Ref: Standard Methods 4500-O G - 2001
Hach Method 10360
In Situ Method 1002-8-2009
ASTM Method D888-09 (B)
ASTM Method D888-09 (C)

Rev. 04/2013

Dissolved Oxygen Meter Calibration Verification

D.O. meters/probes must be calibrated each day of use prior to sample analysis. If the meter cannot be calibrated, the calibration must be verified each day of use. Additionally, when performing D.O. analyses away from the certified laboratory's primary location, a post analysis calibration verification must be analyzed at the end of the run for all types of D.O. probes (LDO sensor and membrane electrode). Below is a procedure for verifying the calibration of a D.O. probe.

1) Follow the manufacturer's instructions for meter operation.
2) Place probe in a plastic bag, the probe storage cup, the storage well of the meter (each containing a wet sponge), or a BOD bottle partially filled with water. Allow appropriate instrument warm up time.
3) Read D.O. and temperature.
4) Check the reading vs. the solubility table below and apply appropriate atmospheric (barometric) pressure or altitude correction factor.
5) Calculated D.O. value must verify meter reading within ± 0.5 mg/L (do NOT calculate and apply a correction factor to calculated D.O.).

Temp. °C	D.O. mg/L		Temp. °C	D.O. mg/L
4	13.11		19.5	9.18
4.5	12.94		20	9.09
5	12.77		20.5	9.00
5.5	12.61		21	8.92
6	12.45		21.5	8.83
6.5	12.30		22	8.74
7	12.14		22.5	8.66
7.5	11.99		23	8.58
8	11.84		23.5	8.50
8.5	11.70		24	8.42
9	11.56		24.5	8.34
9.5	11.42		25	8.26
10	11.29		25.5	8.18
10.5	11.16		26	8.11
11	11.03		26.5	8.04
11.5	10.90		27	7.97
12	10.78		27.5	7.90
12.5	10.66		28	7.83
13	10.54		28.5	7.76
13.5	10.42		29	7.69
14	10.31		29.5	7.62
14.5	10.20		30	7.56
15	10.08		30.5	7.50
15.5	9.98		31	7.43
16	9.87		31.5	7.37
16.5	9.77		32	7.31
17	9.67		32.5	7.24
17.5	9.57		33	7.18
18	9.47		33.5	7.12
18.5	9.38		34	7.07
19	9.28		34.5	7.01

Atmospheric Pressure mm Hg	Equivalent Altitude Ft.	Correction Factor
760	0	1.00
752	278	.99
745	558	.98
737	841	.97
730	1126	.96
722	1413	.95
714	1703	.94
707	1995	.93
699	2290	.92
692	2587	.91
684	2887	.90
676	3190	.89
669	3496	.88
661	3804	.87
654	4115	.86
646	4430	.85
638	4747	.84
631	5067	.83
623	5391	.82
616	5717	.81
608	6047	.80
600	6381	.79
593	6717	.78

Ref: YSI Model 5000/5100 DO Meter Manual. Slight variations in D.O., pressure, and/or altitude may be found in other manuals.

Example: If ambient temperature is 21°C and elevation is approximately 1126 ft, the theoretical D.O. would be:

8.92 X 0.96 = 8.56 mg/L

or, If ambient temperature is 21°C and the atmospheric (barometric) pressure is 745 mm Hg, the theoretical D.O. would be:

8.92 X 0.98 = 8.74 mg/L

NORTH CAROLINA WASTEWATER/GROUNDWATER LABORATORY CERTIFICATION APPROVED PROCEDURE FOR THE ANALYSIS OF pH

This document provides an approved procedure for the analysis of pH per 15A NCAC 2H .0805 (a) (6) (F) and (g) (3).The procedures in this document, in addition to all requirements of the EPA approved method found in 40 CFR Part 136.3, must be met.

HOLDING TIME:

- Samples must be analyzed within 15 minutes of collection (40 CFR Part 136 Table II).

METER CALIBRATION:

- Instruments are to be calibrated according to the manufacturer's calibration procedure prior to analysis of samples each day compliance monitoring is performed.

- Use a pH meter accurate and reproducible to 0.1 pH unit (as demonstrated daily by acceptable performance of a check standard buffer) with a range of 0 to 14 and equipped with temperature-compensation adjustment. The meter must be calibrated with at least two buffers. In addition to the calibration buffers, the meter calibration must be verified with a third standard buffer solution. The calibration and check standard buffers must bracket the range of the samples being analyzed. A portion of the buffer solutions should not be used for more than one calibration. Discard any used buffer portions.

- The check standard buffer must read within ±0.1 S.U. to be acceptable. If the meter verification does not read within ±0.1 S.U., the meter must be recalibrated before any samples are analyzed.

- When performing analyses away from the certified laboratory's primary location, a post analysis calibration verification using the check standard buffer must be analyzed at the end of the run. It is recommended that a mid-day check standard buffer be analyzed when samples are analyzed over an extended period of time. The post analysis check standard buffer(s) must read within ±0.1 S.U or corrective actions must be taken.

General Information:

- Samples shall be gently stirred during measurement. Steps must be taken to eliminate cross contamination between measurements (e.g., rinsing and blotting the electrode dry, dipping the electrode in stream multiple times, etc.).

- The units of measure for pH analyses are Standard Units (S.U.). It is recommended that pH be read in one-hundredths (0.01). Values must be reported in tenths (0.1). It should be noted that many proficiency testing (PT) providers require samples be reported to one-hundredths.

DOCUMENTATION:

The following must be documented in indelible ink whenever sample analysis is performed.

1. Date and time of sample collection.
2. Date and time of sample analysis to verify the 15 minute holding time is met. Alternatively, one time may be documented for collection and analysis with the notation that samples are measured *in situ* or immediately at the sample site.
3. Sample site including facility name and location, ID, etc.
4. Collector's/analyst's name or initials.
5. Meter calibration and meter calibration time(s).
6. True values of buffers used for calibration.
7. True value for the check standard buffer.
8. Value obtained for the check standard buffer (verification of ± 0.1 S.U.).
9. True value and value obtained for the post analysis calibration verification(s), where applicable.
10. Report all data values to the nearest 0.1 pH unit.
11. Traceability for chemicals, reagents, standards and consumables.
12. Instrument identification.
13. Parameter analyzed.
14. Data qualifier(s), when applicable.
15. Equipment maintenance (recommended).

Refer to *Quality Assurance Policies for Field Laboratories* (at http://portal.ncdenr.org/web/wq/lab/cert/field/policy) for additional quality assurance and quality control requirements.

Ref: Standard Methods 4500-H^+ B – 2000 Rev. 04/2013

NORTH CAROLINA WASTEWATER/GROUNDWATER LABORATORY CERTIFICATION APPROVED PROCEDURES FOR THE ANALYSIS OF SPECIFIC CONDUCTANCE (CONDUCTIVITY)

This document provides an approved procedure for the analysis of Specific Conductance per 15A NCAC 2H .0805 (a) (6) (F) and (g) (3). The procedures in this document, in addition to all requirements of the EPA approved method found in 40 CFR Part 136.3, must be met.

Holding Time:

- Samples must be analyzed within 28 days of collection (40 CFR Part 136 Table II).
- Samples must be stored above freezing and ≤6°C, if not analyzed immediately.

General Information:

- In water analysis, the measurement is expressed in µmhos/cm. Some meters display units in µS/cm. (1µmho/cm = 1µS/cm)
- Conductivity samples must not be diluted.
- When performing analyses away from the certified laboratory's primary location, a post analysis calibration verification must be analyzed at the end of the run. It is recommended that a mid-day calibration verification be performed when samples are analyzed over an extended period of time. The value obtained for the post analysis calibration verification check standard must read within 10% of the true value of the post analysis calibration verification check standard. If the obtained value is outside of the ±10% range, corrective action must be taken.
- The Automatic Temperature Compensator (ATC) must be verified annually (i.e., 12 months) at two temperatures by analyzing a standard or sample at 25°C (the temperature that conductivity values are compensated to) and a temperature(s) that brackets the temperature ranges of the environmental samples routinely analyzed. This may require the analysis of a third temperature reading that is > 25°C (see #3 below). The manner in which the ATC is verified may depend upon the meter's capabilities and the manufacturer's instructions. The following is one option.

  1. Pour an adequate amount of conductivity standard or sample into a beaker or other container and analyze at 25°C. Document the temperature and conductivity value.
  2. Lower the temperature of the standard or sample (e.g., by placing the container in a refrigerator or ice chest) to less than the lowest anticipated sample temperature and analyze. Document the temperature and conductivity value.
  3. If samples greater than 25°C are to be analyzed, perform the following additional step: Raise the temperature above 25°C to greater than the highest anticipated sample temperature (e.g., by placing the container in a hot water bath) and analyze. Document the temperature and conductivity value.

  As the temperature increases or decreases, the value of the conductivity standard or sample must be within ±10% of the true value of the standard or ±10% of the value of the sample at 25°C. If not, corrective action must be taken.

  Anticipated temperatures can be obtained from a review of the Discharge Monitoring Reports (DMRs) from the peak summer and winter months. Historical data should provide a reasonably accurate estimation of ranges that will bracket the expected sample temperatures.

  Other certified laboratories may provide assistance in meeting this ATC verification requirement.

Rev. 04/2013

Standards:

Potassium Chloride (KCl) Conductivity standards may be purchased in the ranges desired, or they may be prepared according to Table 2510:I of Standard Methods, 2510 A - 1997. A portion of the standard should not be used for more than one calibration. Discard any used standard portions.

Calibration:

1. Instruments are to be calibrated according to the manufacturer's calibration procedure prior to analysis of samples each day compliance monitoring is performed. For most meters, this is a one-point calibration.

2. Thoroughly rinse cell with one or more portions of sample.

3. Analyze and document a calibration verification check standard prior to environmental sample analysis. It is recommended that this standard value bracket (may be higher or lower than the calibration standard, as applicable) the expected range of sample values measured.

4. The value obtained for the calibration verification check standard must read within 10% of the true value of the calibration verification check standard. If the obtained value is outside of the ±10% range, corrective action must be taken.

Documentation:

The following must be documented in indelible ink whenever sample analysis is performed.

1. Date and time of sample collection.
2. Date and time of sample analysis to verify the 28 day holding time is met. Alternatively, one time may be documented for collection and analysis with the notation that samples are measured *in situ* or immediately at the sample site.
3. Sample site including facility name and location, ID, etc.
4. Collector's/analyst's name or initials.
5. Meter calibration and meter calibration time(s).
6. True value of the standard used for calibration.
7. True value of the calibration verification check standard.
8. Value obtained and time analyzed for the check standard (verification of ± 10% recovery).
9. True value and value obtained for the post analysis calibration verification(s), where applicable.
10. All data must be reported in µmhos/cm at 25ºC or corrected to 25ºC.
11. Traceability for chemicals, reagents, standards and consumables.
12. Instrument identification.
13. Parameter analyzed.
14. Data qualifiers, when necessary.
15. Equipment maintenance (recommended).

Refer to *Quality Assurance Policies for Field Laboratories* (at http://portal.ncdenr.org/web/wq/lab/cert/field/policy) for additional quality assurance and quality control requirements.

Ref: Standard Methods 2510 B – 1997
EPA Method 120.1

Rev. 04/2013

NORTH CAROLINA WASTEWATER/GROUNDWATER LABORATORY CERTIFICATION APPROVED PROCEDURE FOR THE ANALYSIS OF TEMPERATURE

This document provides an approved procedure for the analysis of Temperature per 15A NCAC 2H .0805 (a) (6) (F) and (g) (3). The procedures in this document, in addition to all requirements of the EPA approved method found in 40 CFR Part 136.3, must be met.

HOLDING TIME:

- Immediate (i.e., *in situ*) analysis is required (40 CFR Part 136 Table II).
- When analyzing samples at a site where *in situ* analysis will interfere with obtaining an accurate reading due to conditions present (e.g., low flow, etc.), it is acceptable to collect the sample in a container and analyze on site.
- When analyzing samples in a hazardous area (such as some highway bridges, etc.), the samples should be transported and analyzed at a safe location near the collection point.

GENERAL INFORMATION:

- Temperature measurements must be made with a Celsius thermometer or other acceptable temperature-measuring device. Infrared (IR) devices are not acceptable for compliance monitoring. It is recommended that all liquid-in-glass thermometers have a metal case to prevent breakage.
- A Conductivity, Dissolved Oxygen, pH or multi-parameter meter with a temperature sensing device may be used to measure and document temperature for compliance monitoring.
- The number of decimal places that the measurement is reported to will determine the degree increments required for the temperature measuring device. Standard Methods 2550 B – 2000 states that the thermometer should have a scale indicated for every 0.1ºC. This is required for all measurements performed to tenth degree increments. (e.g., 24.7ºC). If measurements are reported in whole numbers, a temperature measuring device having a scale indicated for every 1ºC is adequate (e.g., 22ºC).
- Unless greater precision is required by the permit or data receiving agency, it is recommended that all temperatures reported for compliance monitoring, be reported in whole numbers. It should be noted that many vendors require proficiency testing (PT) samples be reported to two decimal places.
- All thermometers and temperature measuring devices must be checked **every 12 months** against a National Institute of Standards and Technology (NIST) traceable thermometer. The process must be documented and proper corrections made to all compliance data. To check a thermometer or the temperature sensor of a meter, read the temperature of the thermometer/meter against a NIST traceable thermometer and record the two temperatures. The verification must be performed in the approximate range of the sample temperatures measured. The thermometer/meter readings must be **less than or equal to 1ºC** from the NIST traceable thermometer reading. The documentation must include the serial number of the NIST traceable thermometer that was used in the comparison. Also document any correction that applies on both the thermometer/meter and on a separate sheet to be filed. (NOTE: Other certified laboratories may provide assistance in meeting this requirement.)
    - NIST traceable thermometers used for temperature measurement must be recalibrated in accordance with the manufacturer's recalibration date. If no recalibration date is given, the NIST traceable thermometer must be recalibrated annually.
    - NIST traceable thermometers used to verify the calibration of other thermometers or temperature sensors (i.e., limited use only) must be recalibrated in accordance with the manufacturer's recalibration date and the process documented. If no recalibration date is given, the NIST traceable thermometer must be recalibrated every 5 years.

Rev. 04/2013

DOCUMENTATION:

The following must be documented in indelible ink whenever sample analysis is performed.

1. Date and time of sample collection.
2. Date and time of sample analysis. Alternatively, one time may be documented for collection and analysis with the notation that samples are measured *in situ* or immediately at the sample site.
3. Sample site including facility name and location, ID, etc.
4. Collector's/analyst's name or initials.
5. Document sample temperature measurements with any applicable temperature corrections applied.
6. All data must be reported in °C.
7. The temperature correction (even if it is zero) must be posted on the meter as well as in hard copy format (to be retained for 5 years).
8. Annual calibration verification against an NIST traceable thermometer.
9. Thermometer/instrument identification.
10. Parameter analyzed.
11. Data qualifiers, when necessary.
12. Equipment maintenance (recommended).

Refer to *Quality Assurance Policies for Field Laboratories* (at http://portal.ncdenr.org/web/wq/lab/cert/field/policy) for additional quality assurance and quality control requirements.

Ref: Standard Methods 2550 B - 2000.

Rev. 04/2013

INTENSIVE SURVEY BRANCH
STANDARD OPERATING PROCEDURES MANUAL:
PHYSICAL AND CHEMICAL MONITORING

Version 2.1
December 2013

This document has been approved for release by:

Jason Green — Date 12/10/2013
Supervisor, Intensive Survey Branch

Dianne M. Reid — Date 12/11/13
Chief, Environmental Sciences Section

N.C. DEPARTMENT OF ENVIRONMENT AND NATURAL RESOURCES

DIVISION OF WATER RESOURCES

ENVIRONMENTAL SCIENCES SECTION

ISB STANDARD OPERATING PROCEDURES

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INTRODUCTION

This manual contains the standard operating procedures (SOP) employed by the North Carolina Division of Water Resources (DWR) to evaluate water quality. It is intended to encompass all aspects of routine physical and chemical water quality monitoring with the occasional sediment samples. Therefore, this manual is to be considered a working, dynamic guideline for DWR personnel. Efforts to improve current procedures will continue, and the manual will be revised periodically, as needs dictate.

The primary goal of the manual is to promote the use of procedures that are consistent and reliable during field operations. All employees of the DWR staff are expected to be familiar with and to utilize these procedures as appropriate tools for water quality data collection. Because the procedures have been presented to cover a broad range of applications encountered in water quality monitoring, modifications may be necessary for specific conditions. Deviations from the procedures outlined in this manual, however, should be documented at time of collection.

These standard operating procedures apply to surface water, waste water, and sediment. The manual details procedures for sample collection and handling, as well as methods for parameters that must be measured in situ.

Procedures are referenced at the end of each section. In addition, all references are compiled in Section XIII. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the Division of Water Resources.

These standard operating procedures will assist the Division of Water Resources in its efforts to monitor the waters of the state with increased accuracy and confidence.

TABLE OF CONTENTS

ISB STANDARD OPERATING PROCEDURES

FIGURES

INTENSIVE SURVEY BRANCH PROCEDURES DOCUMENT REVIEW LOG

SOP Name: **Intensive Survey Branch Standard Operating Procedures Manual: Physical and Chemical Monitoring**

Version: 2.1

Revised: December 10, 2013

Jason Green — Prepared By: — 12/10/2013 — Date

Jason Green — Branch Approval By: — 12/10/2013 — Date

Dianne M. Reid — Section Approval By: — 12/11/2013 — Date

Completed hard copy & signed original maintained by ISB Supervisor

DOCUMENT READ BY:			
Name (print):	Date Read:	Version Read:	Signature:

Completed hard copy maintained by ISB Supervisor

INTENSIVE SURVEY BRANCH SOP REVISION LOG

Date	Version Edited	Chapter	Changes	Name
12-10-13	Ver 2.0	Cover page	Updated document date & version to Decemberr 2013 and Version 2.1	Jason Green
12-10-13	Ver 2.0	Cover page & Review Log	Updated Section Chief to Dianne M. Reid	Jason Green
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12-10-13	Ver 2.0	II. 4	Updated Figure 10. – Meter Calibration Sheet	Joanna Gmyr
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12-10-13	Ver 2.0	IV. 1	Addition of sample temperature blank and sample viability upon delivery	Jason Green
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12-10-13	Ver 2.0	Appendix	Added Appendix 7 – Flow Measurement Field Sheet	Jason Green
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11-10-11	Ver 1.3	Entire	Reformatted bullets and lists	Danielle Mir
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03-10-08	Ver 8/2003	2	Updated and changed all calibration/ added QA guidance documents and current equipment type	Danielle Mir
03-10-08	Ver 8/2003	3	Changed parameter holding times & sample methods	Danielle Mir
03-10-08	Ver 8/2003	1	Added additional information on sampling types	Danielle Mir
03-10-08	Ver 8/2003	15	Removed Chapter- conductivity standards must be from certified lab	Danielle Mir
03-10-08	Ver 8/2003	5	Added methods for sediment toxicity samples	Danielle Mir
08-19-08	Ver 8/2003	2 & 11	Put chapter 11 as a section in chapter 2	Danielle Mir

12-10-08	Ver 8/2003	Entire	Changed all Figure numbers	Danielle Mir

I. CONSIDERATIONS FOR WATER QUALITY SAMPLING

The purpose for collecting water samples is to obtain a representative portion of the material or medium being evaluated. Valid results depend upon:

- Ensuring that the sample obtained is a true representative of the material or medium being evaluated;
- Employing proper sampling, handling, and preservation techniques;
- Properly identifying the collected samples and documenting their collection in permanent field records;
- Maintaining sample chain-of-custody procedures, if necessary;
- Protecting the collected samples by properly packing and transporting (shipping) them to the appropriate laboratory for analysis.

1. GENERAL WATER QUALITY SAMPLING CONSIDERATIONS

The following factors and procedures shall be considered and/or implemented in planning and conducting all water quality sampling operations. All of these factors and procedures should be considered in view of the specific objectives and scope of each individual field investigation. It is advisable to discuss sampling with the DWR Chemistry Lab during the planning process to verify and coordinate methodologies, analytical capabilities and timing of sample submittal.

1.1. Selection of parameters to be measured

The parameters to be measured are usually dictated by the purpose of an investigation and should be selected based upon required monitoring conditions (NPDES permits for example) or upon the investigator's knowledge of the problem.

1.2. Dissolved and particulate sample fractions

A sample is generally composed of dissolved and particulate fractions. When it is necessary to analyze samples for individual fractions, it is necessary to filter the sample in the field (i.e. dissolved phosphorous).

1.3. Required sample volumes

The volume of sample obtained should be sufficient to perform all the required analyses with an additional amount collected to provide for any quality control needs such as split samples or repeat examinations. DWR Laboratory sample submitting guidance document can be found at: http://portal.ncdenr.org/c/document_library/get_file?uuid=92a278e5-f75a-4e42-9be5-282ac0216b2a&groupId=38364.

1.4. Sample handling

After collection, all samples should be handled as little as possible. All personnel should use extreme care to ensure that samples are not contaminated. If samples are placed in an ice chest, personnel should ensure that the ice does not submerge the sample containers, thereby preventing cross-contamination. This is extremely important, especially if the samples are to be used in an enforcement action. Alternatives that can be used to prevent contamination include the use of frozen water

containers instead of ice or double wrapping the sample containers in trash bags surrounded with ice.

1.5. Special precautions for sampling trace amounts of contaminants

Most contaminant compounds are detected in the range of parts per billion or parts per trillion; therefore, extreme care must be taken to prevent contamination of samples. The following precautions shall be taken when trace contaminants are of concern:

1.5.1. When sampling surface waters, the aqueous sample should always be collected prior to any sediment sample collection. Sample collection should always be performed using cleaned equipment and proper collection technique.

1.5.2. Sample collection activities should proceed progressively from the least contaminated area to the most contaminated area (if this fact is known).

1.5.3. When possible, samples should be collected facing upstream to avoid contamination from sampling activities.

1.6. Procedures for identifying potentially hazardous samples.

1.6.1. Samples that are either **known** or **thought** to be **hazardous** should be identified **clearly** on both the sample tag and field sample sheet.

1.6.2. Information explaining the hazard, i.e., corrosive, flammable, poison, etc., shall also be listed.

1.6.3. If a sampling hazard is identified, only continue if a properly trained staff member is present and if appropriate safety equipment are available.

1.6.4. Follow procedures found on the ESS Fish Kill web page when sampling fish kill events: http://portal.ncdenr.org/web/wq/ess/fishkills

1.7. Collection of auxiliary data

All auxiliary data, such as flow measurements, photographs of sampling sites, meteorological conditions, and other observations, shall be entered into field records at the time samples are collected.

1.8. Time records

All records of time shall be kept utilizing local time in the military (2400 hour) time format and shall be recorded to the nearest five (5) minutes unless more precise measurements are dictated.

1.9. Transporting and shipping of samples

Samples may be hand delivered to the appropriate laboratory, or they may be shipped by common carrier. Chain of custody may be necessary during and after sample collection (Chapter II.3). All personnel must be aware that certain samples could be classified as hazardous materials and as such, could be regulated by the U.S. Department of Transportation under the Transportation Safety Act of l974. These regulations are contained in Title 49, CFR, Parts ll0-ll9 (An example would be concentrated acid, azide, etc.). A copy of these regulations is available online at: http://www.gpoaccess.gov/cfr/index.html.

I. CONSIDERATIONS FOR WATER QUALITY SAMPLING

2. SURFACE WATER SAMPLE SITE SELECTION

Selection of a surface water sampling location for water quality studies is based on many factors. These include but are not limited to, study objective, water use, point source discharges, non point source discharges, tributaries, changes in stream characteristics, types of stream bed, stream depth, turbulence, presence of structures (weirs, dams), accessibility, safety concerns, and personnel. When such sampling locations are located in estuarine systems, tidal effects must be considered when determining sampling locations.

Before sampling is conducted, a site assessment should be conducted to locate suitable sampling locations. Bridges and piers are normally good choices as they provide ready access and permit water sampling at any point across the width of the water body. When sampling from bridges, samples should be taken from the upstream side; however, this may alter the nature of water flow and cause sediment deposition. Additionally, bridges and piers are not always located in desirable locations with reference to waste sources, tributaries, etc. Wading for water samples is not recommended in lakes, ponds, and slow-moving rivers and streams. However, when wading for sample collections in slow-moving water bodies, it is best to work from downstream stations to upstream sampling points, especially when samples are taken in close proximity. In slow-moving or deep water, a boat is usually required for sample collections and sampling should allow for the possible presence of stratification.

3. SAMPLE COLLECTION TYPES

3.1. Grab sample

A grab sample is a sample collected over a period of time not exceeding 15 minutes. A grab sample is normally associated with water or wastewater sampling. However, soil, sediment, liquid hazardous waste samples, etc., may also be considered grab samples; no particular time limit would apply for the collection of such samples. These samples are used to characterize the medium at a particular point in time; and are generally associated with instantaneous water or wastewater flow data.

3.1.1. *Conditions when a grab sample is conducted*

a. Water or wastewater stream is not continuous (e.g., batch discharges or intermittent flow);
b. Characteristics of the water or waste stream are known to be constant;
c. Sample is to be analyzed for parameters whose characteristics are likely to change significantly with time (i.e., dissolved gases, bacteria, etc.);
d. Sample is to be collected for analysis of a parameter such as oil and grease where the compositing process could significantly affect the observed concentrations;
e. Data on maximum/minimum concentration are desired for a continuous water or wastewater stream;
f. When NPDES permit effluent monitoring specifies grab collections.

3.1.2 *Grab sample collection methods*

A grab sampler is collected at 0.15 m below the water surface. Gloves should be warn for personal safety and to prevent sample contamination.

a. Direct- A sample bottle is placed 0.15 m below the water surface while pointing the bottle mouth up current or towards the bow of a boat when lake sampling.

b. Intermediate Grab Sampling Device- These devices are any type of sampling device that holds the sample prior to pouring it into a sample bottle, and are used when sampling from a bridge or area that the water cannot be reached. The collection end is placed 0.15 m below the water's surface with the open end facing upstream or up current. An example is a Polyethylene Dipper (Figure 1) or other custom-made devices.

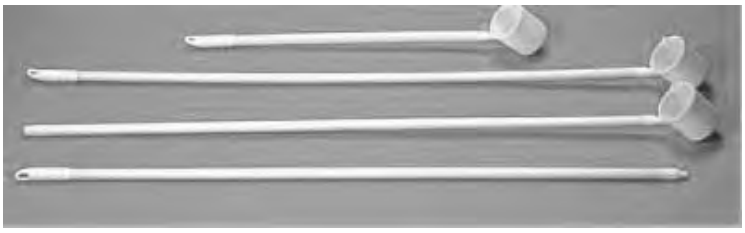


Figure 1. Polyethylene dipper typically used by DWR.

3.1.3. *Parameters that are always grab samples:*

metals	phenol
sulfide	oil and grease
volatile organics	bacterial
chlorine residual	other dissolved gases

3.2. Composite sample

Composite samples are used when average concentrations are of interest and are associated with average flow data (where appropriate). Composite sampling is employed when the water or wastewater stream is continuous or it is necessary to calculate mass/unit time loadings or when analytical capabilities are limited.

3.2.1. *Timed integrated*

A timed integrated composite sample contains discrete samples taken at equal time intervals over the compositing period. A timed composite may be collected continuously. A timed composite is collected continuously or with constant sample volume and a constant time interval between samples.

3.2.2. *Flow proportional integrated*

A flow proportional composite contains discrete samples, taken proportional to the flow rate over the compositing period. Proportional composites are collected with constant sample volume and constant time interval between samples proportional to stream flow.

3.2.3 *Area Integrated*

Area integrated composite samples are collected over a predetermined area of a waterbody, usually from the same depth. Samples are collected then composited into one representative sample.

3.2.4. *Vertical spatial composite (Photic Zone Sampling)*

Vertical spatial samples are composite samples (a.k.a. photo zone, depth-intergraded samples) taken within the photic zone. The photic zone is found between the surface and twice the secchi reading (Chapter III.6). Samples are collected by lowering and raising an integrated depth sampling device such as a Labline water sampler (Figure 2) at a steady speed to obtain a representative water sample within the photic zone. Prior to sampling, the Labline should be rinsed 3 times with station water to avoid sample contamination.

Figure 2. Labline sampler for photic zone (vertical spatial) composites.

3.3. Split sample

A split sample is a sample that has been portioned into two or more containers from a single collection device. Portioning assumes adequate mixing to assure the split samples are, for all practical purposes, identical. Devices such as churn splitters should be rinsed with ambient site water prior to field use for composite split samples, cleaned with phosphorous free cleaner after use and rinsed with deionized water before storage. Composite sample volume in the splitter should allow for ¾ of the total aliquot to be split with ¼ remainder. This prevents aeration of the sample during dispensing. Sample agitation should be performed for 2 minutes prior to sample split to ensure homogeneity of the composite. The spigot or valve should be purged prior to dispensing the first sample. As the composite volume in the churn is reduced, churning rate should increase.

3.4. Duplicate sample

Duplicate samples are collected simultaneously from the same source, under identical conditions but in separate containers.

3.5. Control sample

A control sample is collected upstream or upgrade from a source or site to isolate the effects of the source or site on the particular ambient medium being evaluated according to the study plan for that particular project.

3.6. Background sample

A background sample is collected from an area, water body, or site similar to the one being studied but located in an area known or thought to be free from the pollutants of concern. Background samples should be taken from well-mixed areas, not necessarily midstream to represent normal conditions.

3.7. Sample aliquot

A sample aliquot is a portion of a sample that is representative of the entire sample.

3.8. Scoop sample

A scoop sample is one that is taken in a non-quantitative way for identification only, such as a surface skim, a filamentous clump or rock scrape. All aquatic macrophyte samples are taken as scoop samples.

3.9. Physical Water Quality Measurements (In-Situ Field Measurements)

Physical parameter measurements recorded by a field meter such as a Hydrolab or YSI. Parameters that are considered physical water quality samples or parameters are:

Depth (m)	Temperature (°C)
Salinity (ppt)	Conductivity (us)
pH	Dissolved Oxygen (mg/L)

These may be measured at various depths depending on the water body and needs of the study being performed.

I. CONSIDERATIONS FOR WATER QUALITY SAMPLING

4. AUTOMATIC SAMPLERS

The Instrumentation Specialties Company (ISCO) model 2700 (Figure 3) and model 3700 wastewater samplers are portable devices designed to collect up to 24 separate sequential samples or can be programmed for composite sampling.

More complex sampling such as multiplexing, storm spaced sampling, interfacing with a variety of equipment such as flow meters, field printers, and lap top computers can also be accomplished with the 3700 model. Both sampler models must be supplied with 12 VDC power from one of four sources: an ISCO AC power pack, an ISCO nickel-cadmium battery pack, an ISCO sealed lead acid battery, or an external 12 V direct current source (such as an automotive or marine battery).

Refer to the ISCO 2700 and 3700 instruction manuals for detailed description of operating procedures. **It is important to verify the configuration of these samplers prior to placing them in the field** (Instrument Specialties Company 1988, 1991).

Figure 3. ISCO automated samplers.

I. CONSIDERATIONS FOR WATER QUALITY SAMPLING

5. MANUAL SAMPLING

Manual sampling is usually employed when collecting grab samples and immediate *in-situ* field analyses samples. However, it may also be used, in lieu of automatic - equipment, over extended periods of time for composite sampling.

5.1. Manual Sampling Technique:

The best method to manually collect a sample is to use the actual sample container. This eliminates the possibility of contaminating the sample with an intermediate collection container. **The actual sample container must always be used for collecting oil and grease and bacterial samples**.

5.1.1. If the water or wastewater stream cannot be physically reached, an approved intermediate sampling device may be used. Approved intermediate sampling devices include Labline samplers or Van Dorn type samplers. When a sample collected needs to be collected in the sample container such as grease or oil, a cage sampler can be used of the out-of-reach locations (Figure 4).

Figure 4. Cage sampler used in the DWR Ambient Monitoring Program

5.1.2. Collect the sample by lowering a properly cleaned collection vessel (bottle or intermediate sampling devise) into the water or wastewater stream. If an intermediate sampling device is used, the container employed to collect the initial sample must be rinsed three times with sample water and must be constructed of a material that meets requirements of the parameter(s) being investigated. The collection vessel may be lowered by hand or attached to a pole or rope and then lowered into the stream.

5.1.3. Some types of analyses require the use of a pump when sampling. If a pump is used, it is imperative that it be pre-purged and all components of the pump that come into contact with the liquid be properly cleaned to ensure the integrity of the sample.

5.1.4. Tip the collection container into the water or wastewater stream so that the mouth of the container faces upstream.

5.1.5. Rinse out the container via this procedure at least twice before the sample is collected (exceptions to this rinsing procedure may exist if preservatives are present in the sampling container and for certain analyses such as oil and grease).

6. SPECIAL SAMPLE COLLECTION PROCEDURES

6.1. Priority pollutants

6.1.1. Priority pollutant detection limits are usually in the range of parts per billion, thus extreme care must be exercised to ensure sample integrity.

6.1.2. All containers, composite bottles, tubing, etc., used in priority pollutant sample collection should be cleaned as described in Chapter VI.

6.1.3. When possible, the sample should be collected directly into the appropriate sample container. If the material to be sampled cannot be physically reached, an intermediate collection device may be used. This device should be a Teflon, glass or stainless steel vessel or Teflon tubing via a peristaltic type pump. The device should be cleaned as described in Chapter VI.

6.1.4. When an automatic sampler is employed for priority pollutant collection, the procedures described in Chapter I concerning collection of organic and metal samples with automatic samplers should be used.

6.2. Bacterial sampling

Samples for bacterial analysis should always be collected directly into the prepared glass or plastic sample container. Everything possible must be done to avoid contamination through physical contact with the inside of the cap or bottle and mouth of the bottle.

6.2.1. Hold the bottle near the base.

6.2.2. With cap still on, plunge the bottle, neck downward, below the surface and turn until the neck points slightly upward. The mouth should be directed toward the current.

6.2.3. Uncap the bottle and fill to within one inch of the top without rinsing

6.2.4. Recap immediately while underwater.

6.3. Immiscible liquids/oil and grease

Oil and grease may be present in wastewater as a surface film, an emulsion, a solution, or as a combination of these forms. **The designated sample container must always be used for collecting oil and grease samples.**

As it is very difficult to collect a representative oil and grease sample, the inspector must carefully evaluate the location of the sampling point. The most desirable sampling location is the point where greatest mixing occurs. Quiescent areas should be avoided. Because losses of oil and grease will occur onto the sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentrations over an extended period.

6.4. Volatile Organics Analyses (VOA)

Samples to be analyzed for volatile organics should be stored in the appropriate vials to prevent contamination and loss of sample. To verify proper sample container requirements, consult the DWR Chemistry Laboratory website (http://portal.ncdenr.org/web/wq/lab/staffinfo). The current methodology calls for 40 ml screw cap septum vials with a Teflon-silicone disk in the cap. The disks should be placed in the caps (Teflon side down) in the laboratory prior to the initiation of the sampling activities. Extra disks should be carried during field sampling in case of loss of the disks previously placed in the caps.

When there is no chlorine present in the sampled waterbody a 40ml VOA vial pre-preserved with 1:1 HCL by the Central Laboratory should be used for collection. A VOA sample should be preserved with ascorbic acid and 1:1 HCL whenever there is chlorine present or if it is not known if chlorine is present. Chapter 4 section 3.3.2 describes collection method used.

7. WASTEWATER SAMPLING

7.1 General considerations

Important procedures for obtaining a representative wastewater sample include:

a. Collecting the sample at a location where the wastewater is mixed. Therefore, the sample should be collected near the center of the flow channel, at a depth between 0.4 - 0.6 m total depth, where the turbulence is at a maximum and the possibility of solids settling is minimized. Skimming the water surface or dragging the channel bottom should be avoided.
b. Doing cross-sectional sampling when sampling from wide conduits or within a mixing zone. Dye may be used as an aid in determining the most representative sampling point(s).
c. If manually compositing a sample, thoroughly mix individual samples before pouring the individual aliquots into the composite container.

7.1.1. Site selection

Where applicable, wastewater samples should be collected at the location specified in the NPDES permit.

a. Influent - Influent wastewaters are preferably sampled at points of highly turbulent flow in order to ensure adequate mixing.

b. Effluent - Effluent samples should be collected at the site specified in the permit, or if no site is specified, below all treatment units including post aeration.

c. Pond and lagoon sampling - Generally, composite samples should be employed for the collection of wastewater samples from ponds and lagoons. Even if the ponds and lagoons have a long retention time, composite sampling is necessary because of the tendency of ponds and lagoons to short circuit. However, if dye studies or past experience indicate a homogenous discharge, a grab sample may be taken as representative of the waste stream; but in all cases, sampling should be consistent with permit requirements.

7.1.2 Sampling techniques

All techniques are covered in Section IV ISB Standard Operating Procedures and in the NPDES Compliance Sampling Inspection Manual.
http://www.epa.gov/compliance/resources/publications/monitoring/cwa/inspections/npdesinspect/npdesmanual.html

II. FIELD MONITORING

1. DATA SHEETS

There are two types of sheets needed for sample collection. A Field Sheet is used to document sample location and field parameters such as dissolved oxygen, temperature, pH, and secchi depth. A Lab Form is used to submit a sample(s) to the DWR Chemistry Laboratory.

1.1. Field Data Sheets (Figure 5)

These sheets have spaces for the information that identifies the station (station number, station name, date, and comments), sampler, lake observation (wind direction, rain, percent as well as providing spaces for conducting a depth profile by parameter. Data sheets can be found with the project manager (*i.e*. Ambient Lakes Coordinator).

a. Use a pen to mark on the sheets. Make sure that whatever is used is waterproof.
b. Write legibly and within the allotted space.
c. These forms are retained by the sampler for use in writing up the results or may be filed for later use.

1.2. Lab Sheets (Figure 6)

a. These forms are obtained by accessing the DWR's Chemistry Lab website:
http://portal.ncdenr.org/web/wq/lab/staffinfo/samplesubmit/forms
b. A separate form is used for sediment, soil and tissue. Access the DWR Chemistry website to acquire the appropriate lab form. Contract labs will have their own; consult lab prior to sampling for any special requirements.
c. Lab sheets have spaces for all the information that identifies the station and sampler as well as boxes to check indicating the types of analyses to be conducted on the samples from the station.
d. The sample number used on the tags should be entered into the matching Lab Sheet. There is only one sample number per station – it should be recorded on the Lab Sheet and all the samples related to that Lab Sheet. There is only one lab sheet per station.
e. Be sure to secure lab sheets(s) in a watertight container before shipping.
f. After analysis is complete and the information is transcribed to the lab sheet, it will be returned to the sampler.

WATERBODY: _____

COLLECTORS: _____

METER USED : _____
(Sonde SN)

WEATHER CONDITIONS:

Wind Direction: _____

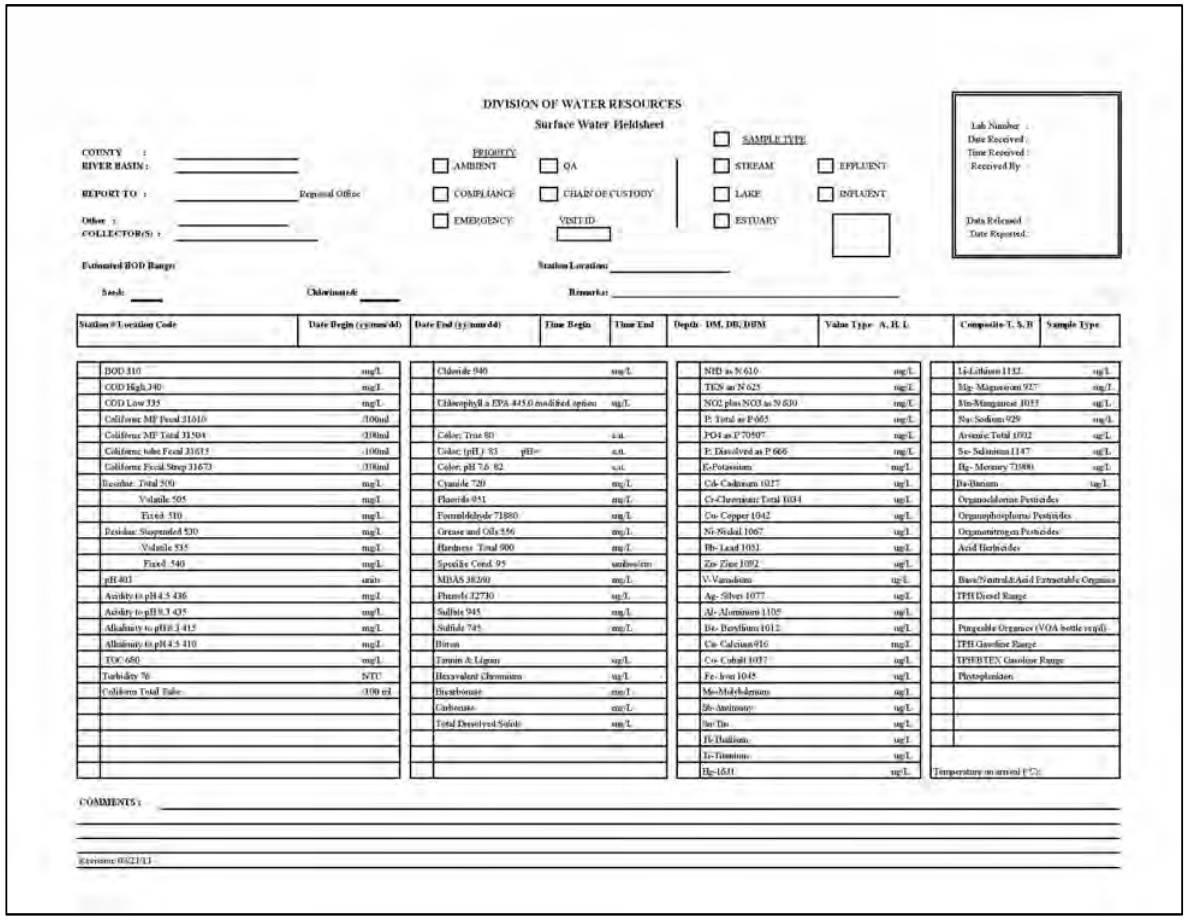
Air Temperature	Wind Velocity	Rainfall (last 48 hrs)
___ < 60°	___ < 10 mph	___ None
___ 60° - 75°	___ 10 - 20 mph	___ < 1/4 inch
___ 75° - 90°	___ > 20 mph	___ 1/4 - 1 inch
___ > 90		___ > 1 inch

STRATIFIED FIELD DATA

STATION NUMBER	DATE YY	MM	DD	TIME (24 hour)	DEPTH (meters) X.XX	TEMP. (°C) x.x	DO (mg/L) x.x	%DO Sat x.x	pH (s.u.) x.x	COND. (umhos/cm) x	SECCHI (meters) x.x	Cloud Cover %	COMMENTS (i.e., water color, algae bloom, sedimentation, lake level fish kill or distress, macrophytes, land disturbance , etc.)

rev 4 April 2, 2013

Figure 5. Stratified Field Data Sheet



DIVISION OF WATER RESOURCES

Surface Water Fieldsheet

COUNTY :
RIVER BASIN :
REPORT TO : Regional Office
Other :
COLLECTOR(S) :

PRIORITY
☐ AMBIENT ☐ QA
☐ COMPLIANCE ☐ CHAIN OF CUSTODY
☐ EMERGENCY VISIT ID

SAMPLE TYPE
☐ STREAM ☐ EFFLUENT
☐ LAKE ☐ INFLUENT
☐ ESTUARY

Lab Number :
Date Received :
Time Received :
Received By :

Data Released :
Date Reported :

Estimated BOD Range:
Station Location:
Seed:
Chlorinated:
Remarks:

Station # Location Code	Date Begin (yy/mm/dd)	Date End (yy/mm/dd)	Time Begin	Time End	Depth - DM, DB, DBM	Value Type - A, H, L	Composite-T, S, B	Sample Type

	BOD 310	mg/L		Chloride 940	mg/L		NH3 as N 610	mg/L		Li-Lithium 1132	ug/L
	COD High 340	mg/L					TKN as N 625	mg/L		Mg- Magnesium 927	mg/L
	COD Low 335	mg/L		Chlorophyll a EPA 445.0 modified option	ug/L		NO2 plus NO3 as N 630	mg/L		Mn-Manganese 1055	ug/L
	Coliform MF Fecal 31616	/100ml					P- Total as P 665	mg/L		Na- Sodium 929	mg/L
	Coliform MF Total 31504	/100ml		Color: True 80	c.u.		PO4 as P 70507	mg/L		Arsenic Total 1002	ug/L
	Coliform tube Fecal 31615	/100ml		Color: (pH / 83 pH=	s.u.		P- Dissolved as P 666	mg/L		Se- Selenium 1147	ug/L
	Coliform Fecal Strep 31673	/100ml		Color: pH 7.6 82	s.u.		K-Potassium	mg/L		Hg- Mercury 71900	ug/L
	Residue - Total 500	mg/L		Cyanide 720	mg/L		Cd- Cadmium 1027	ug/L		Ba-Barium	ug/L
	Volatile 505	mg/L		Fluoride 951	mg/L		Cr-Chromium Total 1034	ug/L		Organochlorine Pesticides	
	Fixed 510	mg/L		Formaldehyde 71880	mg/L		Cu- Copper 1042	ug/L		Organophosphorus Pesticides	
	Residue - Suspended 530	mg/L		Grease and Oils 556	mg/L		Ni-Nickel 1067	ug/L		Organonitrogen Pesticides	
	Volatile 535	mg/L		Hardness - Total 900	mg/L		Pb- Lead 1051	ug/L		Acid Herbicides	
	Fixed 540	mg/L		Specific Cond. 95	umhos/cm		Zn- Zinc 1092	ug/L			
	pH 403	units		MBAS 38260	mg/L		V-Vanadium	ug/L		Base/Neutral&Acid Extractable Organics	
	Acidity to pH 4.5 435	mg/L		Phenols 32730	ug/L		Ag- Silver 1077	ug/L		TPH Diesel Range	
	Acidity to pH 8.3 435	mg/L		Sulfide 945	mg/L		Al- Aluminum 1105	ug/L			
	Alkalinity to pH 4.5 410	mg/L		Sulfide 745	mg/L		Be- Beryllium 1012	ug/L		Purgeable Organics (VOA bottle req'd)	
	Alkalinity to pH 4.5 410	mg/L		Boron			Ca- Calcium 916	mg/L		TPH Gasoline Range	
	TOC 680	mg/L		Tannin & Lignin	ug/L		Co- Cobalt 1037	ug/L		TPH BTEX Gasoline Range	
	Turbidity 70	NTU		Hexavalent Chromium	ug/L		Fe- Iron 1045	ug/L		Phytoplankton	
	Coliform Total Tube	/100 ml		Bicarbonate	mg/L		Mo-Molybdenum	ug/L			
				Carbonate	mg/L		Sb- Antimony	ug/L			
				Total Dissolved Solids	mg/L		Sn-Tin	ug/L			
							Tl-Thallium	ug/L			
							Ti- Titanium	ug/L			
							Hg-1631	ng/L		Temperature on arrival (°C):	

COMMENTS :

Revision: 03/23/13

Figure 6. Surface Water Lab Sheet

2. SAMPLE TAGS

A sample tag is used for most samples returned to the laboratory for analysis (Figure 7). These tags are usually attached to the sample container by a rubber band. In some cases, particularly with biological samples, the sample tag may be included with or wrapped around the sample. Sample tags should be of material that is waterproof and should be written on with indelible ink. It is very important that these tags are legible.

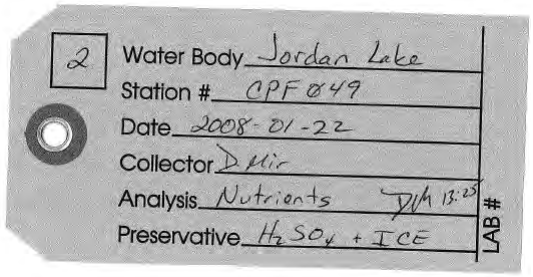


Figure 7. Completed Sample Tag

2.1 Information included on a sample tag:

- Sample number - determined based on number of stations to be sampled that day – All samples from a station will have the same sample number. Figure 7 shows the sample number for the tag as 2.
- Water Body
- Station number
- Date(s) & time(s)
- Name of the person collecting the sample
- Types of analyses to be conducted (such as Nutrients)
- Types of preservatives used
- Sampler initial after preserving with acid

2.2 Responsibility of project leader or field investigator

The project leader or field investigator assigns the station number to be used for that location. If previous sampling has occurred at a site, that station number should be used again. This number is ordinarily a numeric code, designed for a particular study, inspection, or investigation. Ambient stations have a special numbering system. New ambient stations are identified by the Ambient Monitoring Coordinator.

The project leader or field investigator must exercise due caution to ensure that duplicate station numbers are not used during the same study. The project leader or field investigator will also always specify the type of sample collected since the same station number is used when a water and sediment sample is collected at the same location. The exact description of all stations associated with field identification or sample station numbers is documented on the field sheet.

If a sample is split with a facility, state regulatory agency, or other party, sample tags with identical information are to be attached to each of the sample containers; the facility, state regulatory agency, etc., tag shall be marked facility (actual name), state regulatory agency (actual name), etc.

3. CHAIN-OF-CUSTODY PROCEDURES

This procedure is used for samples collected as part of an investigation for legal proceedings or where it is required under the study plan. The possession of samples or other evidence shall be traceable from the time the samples are collected until they are introduced as evidence in legal proceedings.

3.1. Sample Custody

A sample or other physical evidence is under custody if it is in:

- The field investigator's actual possession, or
- The field investigator's view, after being in his/her physical possession, or
- The field investigator's physical possession and then he/she secures it to prevent tampering, or
- A designated secure area.

To simplify the chain-of-custody record and eliminate future litigation problems, as few people as possible should handle the samples or physical evidence. The field investigator is responsible for the care and custody of the samples collected until they are properly transferred to another person or facility.

3.2 Field Custody Procedures

3.2.1 *Security Seal*

a. Complete sample tags for each sample.
b. Place the lab sheets and chain of custody sheets in a Zip-loc bag and place in a cooler along with the samples.
c. Seal the coolers with filament tape and a DWR custody seal similar to the one shown in Figure 8.
d. The field investigator writes the date and their name on the seal. This requirement shall be waived if the field investigator keeps the samples in his custody from the time of collection until they are delivered to the laboratory.

3.2.2 *Chain of Custody Form*

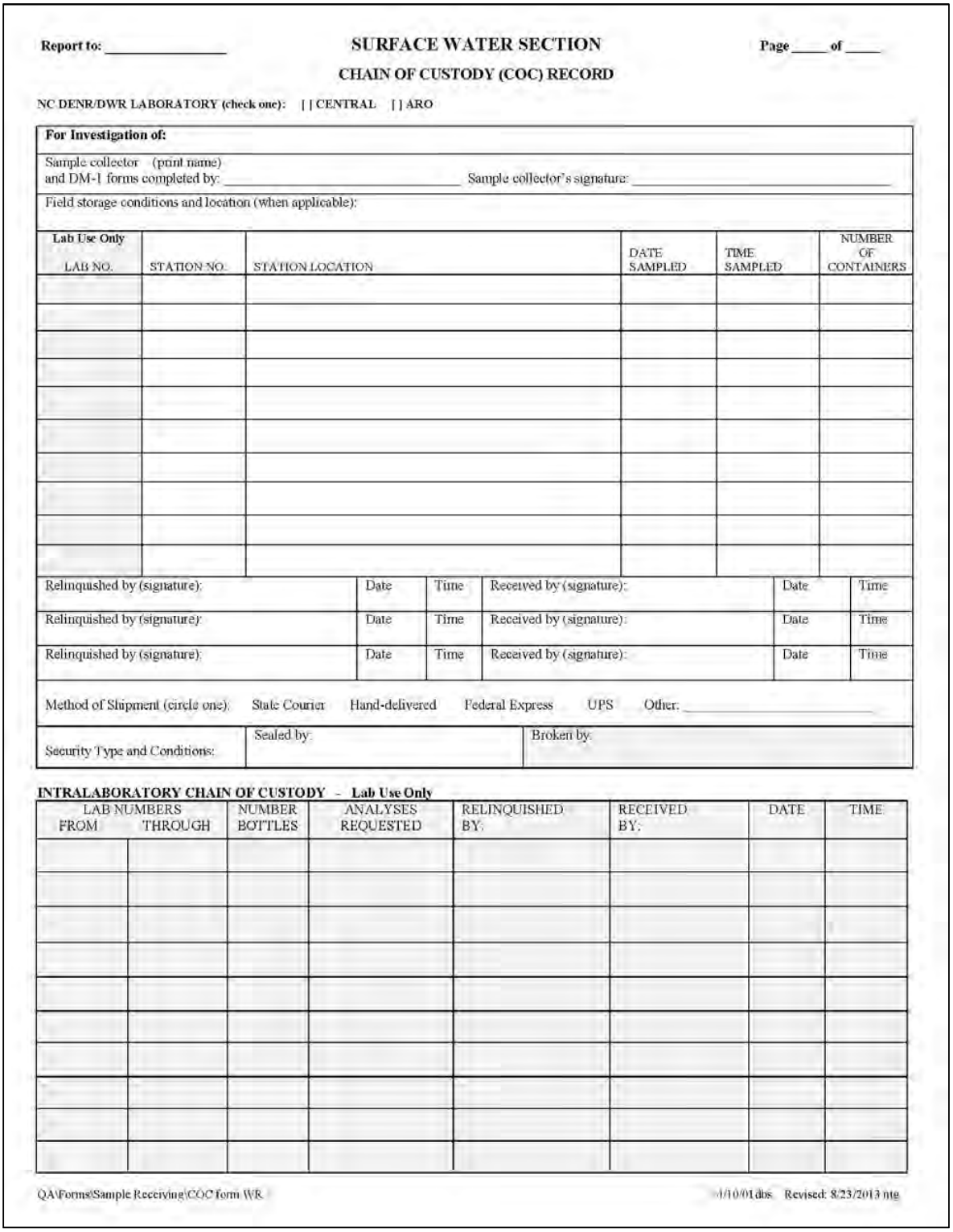
a. Record all samples on the field form or in field logbooks and using the Chain of Custody Record (Figure 9.) available from the DWR Chemistry Lab:

   http://portal.ncdenr.org/web/wq/lab/staffinfo/samplesubmit/forms

b. For documents received during investigations, place them in large envelopes, seal with a DWR seal such that the envelopes cannot be open without breaking the seal and note the contents on the envelope. If at any time the DWR seal is broken, that fact and the reason should be noted on the chain-of-custody record and a new seal affixed. The information on the seal should include the field investigator's signature, as well as the date and time of sealing.
c. Place other physical evidence such as videotapes or other small items in zip-lock bags and affix a DWR seal so that the bag cannot be opened without breaking the seal. A chain-of-custody record should be kept with the items in the bag. Any time the seal is broken, note reason on the chain of custody record and affix a new seal.

d. Personnel shall not accept samples from other sources unless the sample collection procedures used are known to be legally defensible, can be documented, and the sample chain-of-custody can be established. If such samples are accepted, a sample tag and a DWR form, containing all relevant information and the chain-of-custody record, shall be completed for each sample.

Figure 8. DWR Chain of Custody Security Seal



Report to: _____ **SURFACE WATER SECTION** Page ____ of ____

CHAIN OF CUSTODY (COC) RECORD

NC DENR/DWR LABORATORY (check one): [ ] CENTRAL [ ] ARO

For Investigation of:

Sample collector (print name) and DM-1 forms completed by: _____ Sample collector's signature: _____

Field storage conditions and location (when applicable):

Lab Use Only LAB NO.	STATION NO.	STATION LOCATION	DATE SAMPLED	TIME SAMPLED	NUMBER OF CONTAINERS

Relinquished by (signature):	Date	Time	Received by (signature):	Date	Time
Relinquished by (signature):	Date	Time	Received by (signature):	Date	Time
Relinquished by (signature):	Date	Time	Received by (signature):	Date	Time

Method of Shipment (circle one): State Courier Hand-delivered Federal Express UPS Other: _____

Security Type and Conditions:	Sealed by:	Broken by:

INTRALABORATORY CHAIN OF CUSTODY – Lab Use Only

LAB NUMBERS FROM	THROUGH	NUMBER BOTTLES	ANALYSES REQUESTED	RELINQUISHED BY:	RECEIVED BY:	DATE	TIME

QA\Forms\Sample Receiving\COC form WR 1/10/01dbs Revised: 8/23/2013 ntg

Figure 9. Surface Water Section Chain of Custody Form

II. FIELD MONITORING

3.3 Transfer of Custody and Shipment

3.3.1. When transferring the possession of chain of custody samples, the individuals receiving the samples shall sign, date, and note the time that they received the samples on the field form or in the field log book. This action documents transfer of custody of samples from the field investigator to another person (e.g. to the laboratory).

3.3.2. After properly packing samples for shipment to the appropriate laboratory for analysis, secure the shipping containers using nylon strapping tape and custody seals. The seal shall be placed under the point on the tape where the ends are located and wrapped over the top of it. The seal shall be signed, dated, and the time recorded by the field investigator.

3.3.3. Samples split with a facility, state regulatory agency, or other government agency must be signed for on the Chain of Custody Form by the facility, state regulatory agency, or other government agency representative receiving the samples.

3.3.4. All samples shipped shall be accompanied by the DWR chain-of-custody form(s). The original and one copy of the form will be placed in a plastic bag inside the secured shipping container. One copy of the form will be retained by the field investigator or project leader. The original of the form will be transmitted to the field investigator or project leader after samples are accepted by the laboratory.

3.3.5. If sent by mail, the package shall be registered with return receipt requested. If sent by common carrier, a government bill of lading or air bill should be used. Receipts from post offices, copies of bills of lading, and air bills shall be retained as part of the documentation of the chain-of-custody.

4. FIELD INSTRUMENTS

Intensive Survey Branch uses a wide array of instrumentation for recording in-situ water quality parameters. Currently, Hydrolab (Hach Environmental) and YSI (Yellow Springs Instrument Co.) are the main manufacturer's used. Instructions for use, calibration, and maintenance as written by the manufacturer should always be followed. Manufacturers' manuals for all meters can be found in the ESS Calibration Lab. DWR produced a guidance sheet that outlines basic calibration, maintenance, and acceptance criteria for meters commonly used by DWR (Appendices 1-4). **All meter guidelines and guidance sheets found in this document are supplementary to and not a replacement for the manufacturer's directions.**

4.1. All field meters should be calibrated before and checked after sampling activities daily. Calibration data should be documented on a Water Quality Monitoring Field Meter Calibration Sheet (Figure 10).

4.2 In-*situ* field parameter measurements

4.2.1. *Parameters typically measured:*

a. **Conductivity** (µS/cm @ 25 °C)
b. **Dissolved Oxygen** (DO- mg/L)
c. **pH** (Standard Units)
d. **Temperature** (°C)
e. Light Attenuation (µE/m^2/s)

Additional Calibrations and Use of multiparameter Meters

4.2.2. *Battery Voltage*

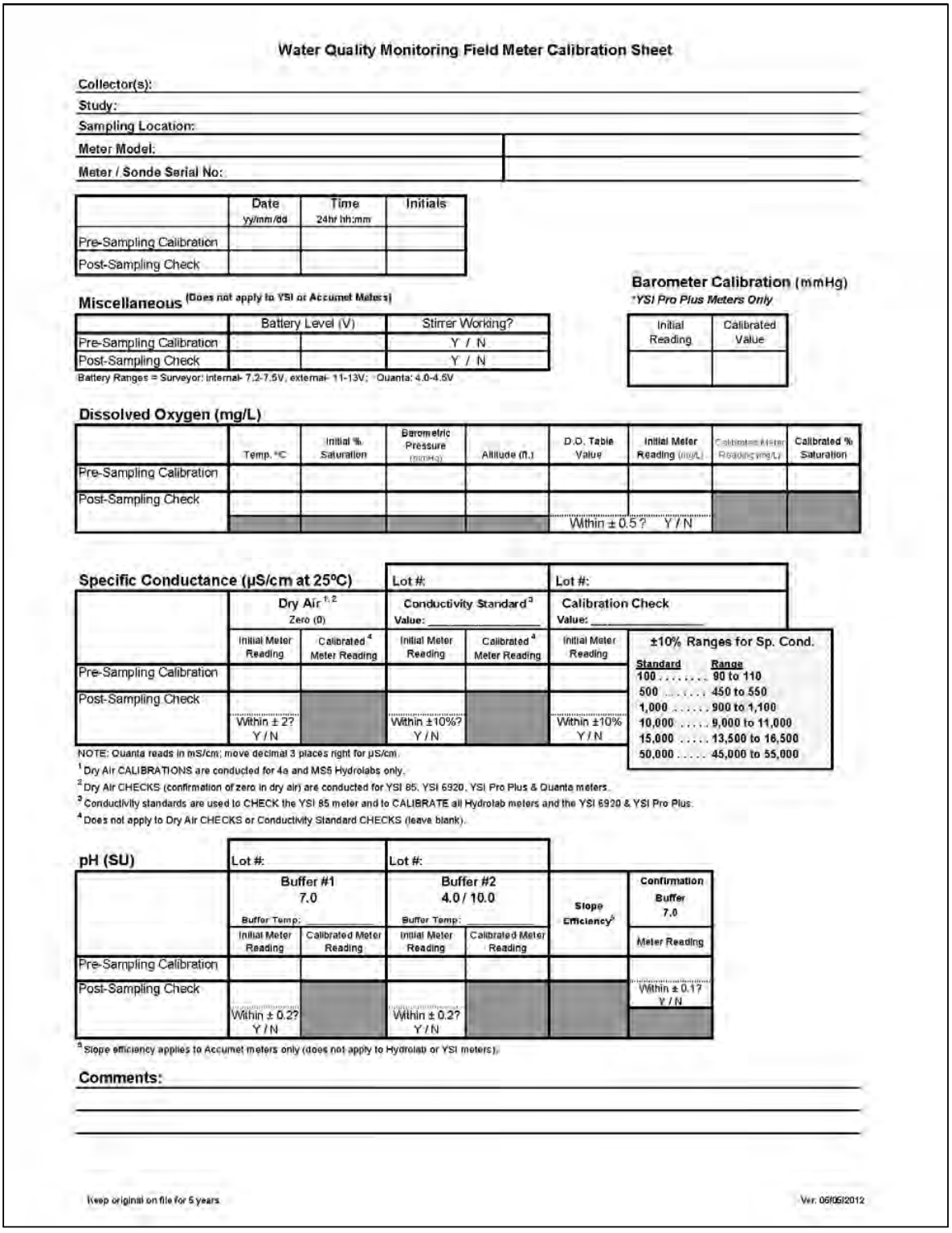
a. Use the correct battery source for the particular instrument in use.
b. Battery voltage must be in an acceptable range before calibrating and using the meter (see respective manual).
c. Record both initial and terminal battery voltage on the Meter Calibration sheet (Figure 10).

4.2.3. *Depth*

a. Some meters can be calibrated to read depth by entering the number zero on the keypad while the sonde sensors are at the surface during field measurements.
b. Record all field depth measurements to the nearest tenth of a meter (if needed).

4.3 Calibrated Backup Field Meters

Although meters are maintained, failure can occur at anytime. Calibrated backup meters, meter manuals, batteries and calibration buffers/ standards are required during sampling. Inability to collect data due to a meter failure is unacceptable. See Appendices 1 – 4 for detailed guidance on using, maintaining, and storage field meters commonly used by DWR.



Water Quality Monitoring Field Meter Calibration Sheet

Collector(s):
Study:
Sampling Location:
Meter Model:
Meter / Sonde Serial No:

	Date yy/mm/dd	Time 24hr hh:mm	Initials
Pre-Sampling Calibration			
Post-Sampling Check			

Miscellaneous (Does not apply to YSI or Accumet Meters)

	Battery Level (V)		Stirrer Working?
Pre-Sampling Calibration			Y / N
Post-Sampling Check			Y / N

Battery Ranges = Surveyor: internal- 7.2-7.5V, external- 11-13V; Quanta: 4.0-4.5V

Barometer Calibration (mmHg)
**YSI Pro Plus Meters Only*

Initial Reading	Calibrated Value

Dissolved Oxygen (mg/L)

	Temp. °C	Initial % Saturation	Barometric Pressure (mmHg)	Altitude (ft.)	D.O. Table Value	Initial Meter Reading (mg/L)	Calibrated Meter Reading (mg/L)	Calibrated % Saturation
Pre-Sampling Calibration								
Post-Sampling Check								
					Within ± 0.5? Y / N			

Specific Conductance (µS/cm at 25°C)

Lot #: Lot #:

	Dry Air [1,2] Zero (0)		Conductivity Standard [3] Value:		Calibration Check Value:	
	Initial Meter Reading	Calibrated [4] Meter Reading	Initial Meter Reading	Calibrated [4] Meter Reading	Initial Meter Reading	±10% Ranges for Sp. Cond.
Pre-Sampling Calibration						Standard / Range 100 . . . . . 90 to 110 500 . . . . . 450 to 550 1,000 . . . . . 900 to 1,100 10,000 . . . . . 9,000 to 11,000 15,000 . . . . . 13,500 to 16,500 50,000 . . . . . 45,000 to 55,000
Post-Sampling Check	Within ± 2? Y / N		Within ±10%? Y / N		Within ±10% Y / N	

NOTE: Quanta reads in mS/cm; move decimal 3 places right for µS/cm.
[1] Dry Air CALIBRATIONS are conducted for 4a and MS5 Hydrolabs only.
[2] Dry Air CHECKS (confirmation of zero in dry air) are conducted for YSI 85, YSI 6920, YSI Pro Plus & Quanta meters.
[3] Conductivity standards are used to CHECK the YSI 85 meter and to CALIBRATE all Hydrolab meters and the YSI 6920 & YSI Pro Plus.
[4] Does not apply to Dry Air CHECKS or Conductivity Standard CHECKS (leave blank).

pH (SU)

Lot #: Lot #:

	Buffer #1 7.0 Buffer Temp:		Buffer #2 4.0 / 10.0 Buffer Temp:		Slope Efficiency [5]	Confirmation Buffer 7.0
	Initial Meter Reading	Calibrated Meter Reading	Initial Meter Reading	Calibrated Meter Reading		Meter Reading
Pre-Sampling Calibration						
Post-Sampling Check	Within ± 0.2? Y / N		Within ± 0.2? Y / N			Within ± 0.1? Y / N

[5] Slope efficiency applies to Accumet meters only (does not apply to Hydrolab or YSI meters).

Comments:

Keep original on file for 5 years.

Ver. 06/05/2012

Figure 10. Meter Calibration Sheet

III. FIELD PARAMETER MEASUREMENTS

1. WATER TEMPERATURE

Temperature measurements are taken by a multiparameter meter (Hydrolab or YSI) or dial Celsius-thermometer or a thermister. Below are some general considerations while collecting water temperature data.

- The meter should have a scale marked for every 0.1°C.
- Make readings with the mulitparameter meter or thermometer in water long enough to permit equilibrium.
- Temperature sensors on the Hydrolab and YSI meters are factory set and do not require recalibration.
- At least once a year check the meter thermometer against a precision thermometer certified by the National Institute of Standards and Technology (NIST).
- Temperature readings must be record as degrees Centigrade (°C) to the nearest tenth of a degree. During field use, the temperature readings should always be read when they are stable and before the other parameters are read to ensure stable readings for all parameters.

2. AIR TEMPERATURE

Refer to previous procedure, except measure the ambient air temperature above the water surface to be sampled. Do not use immersion thermometers to measure air temperature.

3. DISSOLVED OXYGEN

Dissolved oxygen analysis measures the amount of gaseous oxygen dissolved in an aqueous solution. Dissolved oxygen may be measured by electrometric methods (e.g. Hydrolab or YSI) or by chemical methods (Winkler Method).

Testing must be done immediately at the sampling location, as a grab sample, which is why electrometric methods are favored.

See Appendices 1 – 4 for detailed guidance on using, maintaining, and storage of meters and probes commonly used by DWR. **This SOP and the attached meter guidance sheets are supplementary to and not a replacement for the manufacturer's instructions manual.** Manufacturer's operations manuals for all meters are kept in the ESS Calibration Lab.

3.1 Electrometric Method Calibration

All field meters should be calibrated before and checked after sampling activities (at least daily). The calibration data should be entered on a meter calibration sheet (Figure 10). Detailed guidance for calibrating dissolved oxygen is provided in Appendices 1 – 4.

3.1.1 Acceptance Criteria For DO calibration

- Calibrated meters should be compared to the DO table to ensure calibration was done correctly.
- Appendix 5 describes the calculations needed to correct for elevation and a table used at sea-level.
- Dissolved oxygen concentrations need to be calibrated within 0.5mg/L of the elevation corrected table concentration for a given temperature.

3.2. Winkler Method - azide modification (Standard Methods, 18th edition)

The azide modification effectively removes interference caused by nitrite, which is the most common interference in biologically treated effluents and incubated BOD samples. The azide modification is not applicable under the following conditions:

- Samples containing sulfite, thiosulfate, polythionate, appreciable quantities of free chlorine or hypochlorite;
- Samples high in suspended solids;
- Samples containing organic substances which are readily oxidized in a highly alkaline solution or which are oxidized by free iodine in an acid solution;
- Untreated domestic sewage;
- Biological flocs;
- Where sample color interferes with endpoint detection.

In instances where the azide modification is not applicable, electrometric methods should be employed.

Below are some general considerations while collecting dissolved oxygen data using the Winkler Method:

- Collect surface water samples in narrow-mouth glass-stoppered BOD bottles of 300 ml capacity with tapered and pointed ground-glass stoppers and flared mouths. Once analysis is complete and the information is transcribed to the lab sheet, it will be returned to the sampler.
- Avoid entrapping or dissolving atmospheric oxygen. Do not allow the sample to remain in contact with air or be agitated, because either condition may result in a change to its gaseous content.

- Where samples are collected from shallow depths (less than 5 feet) use of an APHA-type sampler is recommended. Use of a Kemmerer type sampler is recommended for samples from depths greater than 5 feet. Bleed sample from bottom of samplers through a tube extending to the bottom of a BOD bottle. Fill bottle to overflowing.
- Record sample temperature to nearest degree Celsius or more precisely.
- Reagents
  - Manganous sulfate solution
  - Alkaline iodide-sodium azide solution.
  - Sulfuric acid (H_2SO_4) concentration
  - Sodium thiosulfate solution 0.025 N
  - Starch solution
- Analysis Steps:
  1. Add 2 mL of manganous sulfate solution to sample container by holding the tip of the pipette below the surface of the liquid.
  2. Add 2 mL of alkaline iodide-sodium azide solution by holding the tip of the pipette below the surface of the liquid.
  3. Replace BOD bottle stopper, avoid trapping air bubbles, and shake well by inversion.
  4. When the precipitate settles, leaving a clear supernatant above the manganese hydroxide floc, shake again.
  5. Allow floc to settle again, at least 200 mL of clear supernate should be above the floc.
  6. Remove the stopper and add 2 mL of concentrated sulfuric acid by holding the pipette above the surface of the liquid and allowing the acid to run down the neck of the bottle, re-stopper, and mix by inversion until no floc is visible.
  7. Withdraw 203 mL of the solution into an Erlenmeyer flask.
  8. Titrate with 0.025 N sodium thiosulfate solution to a pale straw color.
  9. Add 1 mL of starch solution and continue titration to the first disappearance of blue color.
  10. Record the # of mL of thiosulfate used; where 1 mL thiosulfate = 1 mg/L DO.

III. FIELD PARAMETER MEASUREMENTS

4. pH (ELECTROMETRIC METHOD)

4.1. Information on pH

4.1.1. *Precision and accuracy:* ±0.2 pH unit represents the limit of accuracy under normal conditions for measurements of water and poorly buffered solutions. For this reason, report pH values to the nearest 0.1 pH unit. Calibrate instrument within 0.2 pH units of the standard pH buffer value.

4.1.2. *Calibration Reagents* - Calibrate the electrode system against standard buffer solutions of known pH. Always use fresh commercially made buffers to calibrate field meters. Buffer solution and samples should be stored in polyethylene bottles. Never pour decanted or used buffer solution back into the original bottle.

4.1.3 *Procedure* - Always follow the manufacturer's instructions for pH meter storage and preparation of electrodes. Recommended short-term storage of electrodes varies with type of electrode and manufacturer. See Appendices 1 – 4 for detailed guidance on using, maintaining, and storage of pH meters and probes commonly used by ISB. Never store probes in DI water; tap water or pH buffer 4.0 is preferred.

Note: All field meters should be calibrated before and checked after sampling activities daily. The calibration data should be entered on a meter calibration sheet (Figure 10).

4.2. Multiparameter YSI or Hydrolab Meters

The Hydrolab and YSI meters used by ISB all have the same basic method for calibration. A training outline for each meter used by ISB is listed in Appendices 1 - 4. Copies of the manufacturer's instruction manual are located in the ISB calibration room.

4.3. Accumet AP Series (Fisher Scientific) Handheld pH Meters

The Accumet handheld pH meter is a stand-alone pH meter (it does not measure any other parameters beyond pH). See Appendix 2 for detailed guidance on using, maintaining, and storage of the Accumet AP61 pH meter which is typically used in conjunction with the YSI 85 meter. A copy of the manufacturer's instruction manual is located in the ISB calibration room.

5. SPECIFIC CONDUCTIVITY/SALINITY

The specific conductance (conductivity) of a solution is a measure of its ability to carry an electrical current. This ability depends on the presence of ions, their total concentration, mobility, valence, and relative concentrations, and on the temperature of measurement. Specific conductance is the conductance afforded by 1 cc (ml) of a solution of electrolyte and is reported in micromhos per centimeter (µmhos/cm). Specific conductance measurements are used in water analysis to obtain a rapid estimate of the dissolved solids content of a water sample.

5.1 Specific Conductivity Meter Calibration - Detailed meter guidelines for calibrations are listed in Appendices 1 - 4. Copies of manufacturer's instruction manuals are found in the ISB calibration room.

Note: All field meters should be calibrated before and checked after sampling activities daily. The calibration data should be entered on a meter calibration sheet (Figure 10).

5.2 Additional Calibration Information

- *Acceptance Criteria:* Calibrate instrument within ±10% of the calibration standard's true value.
- Always calibrate with fresh, certified conductivity standards.

6. SECCHI DISK TRANSPARENCY

A measurement of water transparency obtained by observing a specially marked, circular disk which is lowered through the water column until it is not visible. This measure of the point at which the disk is non-visible is considered the secchi depth.

6.1. Secchi disk use (Figure 11)

6.1.1. *Conditions for secchi disk readings*

a. Shaded, protected side of boat.
b. Minimal waves or ripples, if possible.
c. Do not wear sunglasses while taking the secchi depth reading.

NOTE: Any departure from these conditions should be specifically stated on the field sheet.

6.1.2. *Method*

a. Rope should be accurately graduated in meters, 0.1 meter graduations for the first meter, 0.5 m graduations thereafter. At a minimum of annually verification of correct graduation is necessary as rope may stretch with continued use.
b. Observer's eye should be 1 meter above the water surface.
c. Lower the disk into the water to the depth at which the disk disappears.
d. Lift the disk and record the depth at which it just reappears.
e. Record the average reading from previous 2 steps on field sheet as Secchi depth reading to the nearest tenth of a meter.

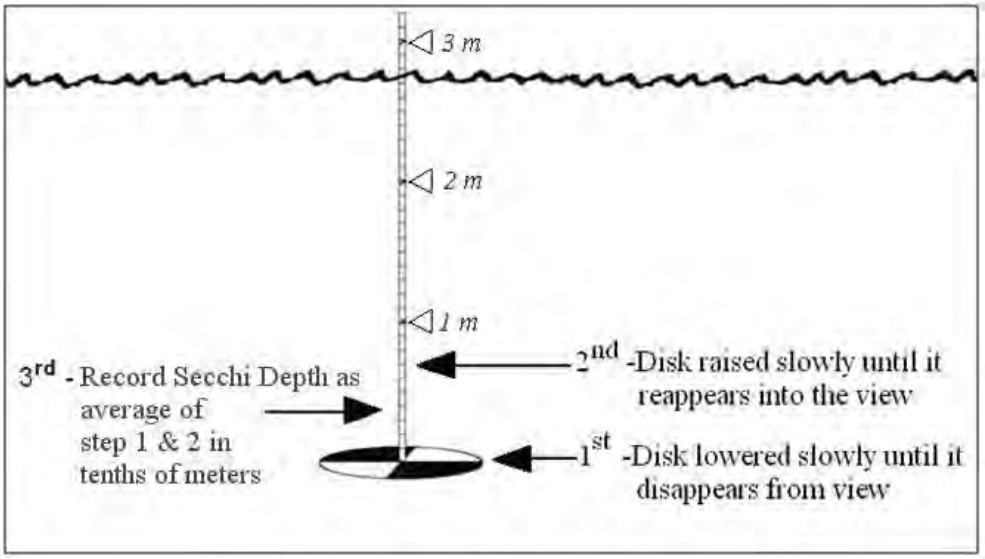


Figure 11. Secchi Disk

7. LIGHT ATTENUATION

The measurement of the decrease in light intensity through the water column as depth increases due to absorption and scattering effects of water molecules.

7.1. Light Attenuation is calculated by obtaining a vertical profile of light, using a PAR (photosynthetically active radiation) meter.

7.1.1. *PAR Meter Preparation*

a. Obtain an independent datalogger such as LI-COR LI-1400.

b. Connect a deck sensor and an underwater sensor to the LI-1400. Make sure the correct calibration factors are entered for each probe. All calibration factors are supplied by the manufacturer.

c. Place the deck sensor on the boat where it will not be shaded.

7.1.2. *Methods*

a. Lower the underwater sensor on the SUNNY, not shaded, side of the boat to a depth about 10 cm to represent the surface.

b. Once readings stabilize, record the values from both sensors ($\mu E/m^2/s$), along with the water depth of the underwater sensor. Log the values in the datalogger.

c. Lower the underwater sensor to 0.5 m (6″), allow the values to stabilize and record the values from both sensors, along with the water depth of the underwater surface.

d. Repeat at the following schedule:
   - Shallow Sites (≤ 2 m) – Every 0.5 m interval;
   - Nominal depths (>2 <10 m) – Every 0.5 m (near surface) and very 1 m interval to near bottom (0.5 m off-bottom)
   - Deep Sites (>10 m) – 0.5 m (near-surface) and every 1 m interval to 10 m, than at 5 m intervals, thereafter, to near-bottom (0.5 m off-bottom)

   NOTE: Follow schedule, unless specified differently for the individual sampling project.

e. If the meter impacts the bottom, allow 2-3 minutes for the disturbed conditions to settle before take the reading.

f. If the light measurements become negative before reaching the bottom, terminate the profile readings at that depth.

8. REFERENCE POINT-TAPE-DOWN MEASUREMENT

Reference point-tape-down is a procedure for determining relative vertical distance between fixed bridge points and stage of a water body below the bridge structure.

8.1. Procedure for Reference Point-Tape-Down

a. Use a weight-tape gage consisting of a graduated (0.1 ft) steel tape to which is fastened a small cylindrical weight (dimwap) of known length.

b. Locate reference point (RP) as documented on the station location sheet. They are often located on the outer edge of bridge railings.

c. Measure by suspending the weight-tape from the reference point (measuring) to the water surface.

d. The reference point value is indicated by direct reading of the suspended tape where it intercepts the fixed reference point. Read from the top of the bevel if the reference point is beveled.

e. Record measurement and add on the length of the weight.

9. STAGE MEASUREMENTS

These procedures are for use at U.S. Geological Survey permanent stream gauging stations.

9.1 Obtaining Stage Measurements

Follow instructions in the USGS publication Stage Measurements at Gauging Stations, Book 3, Chapter A7, United States Department of the Interior, Geological Survey, 1968. http://pubs.usgs.gov/tm/tm3-a7/pdf/tm3-a7.pdf

9.1.1 *Prior to Sampling*

a. Obtain permission from the USGS district chief to read the stage measuring devices in the instrument shelters.

b. Obtain on the job training by USGS personnel as to how to read the stage measuring devices.

9.1.2 *Stage Measuring Devices*

- Staff gage
- Wire weight gage
- Electric-tape instrument
- Automatic digital recorder
- Graphic recorder (bubble meters)

IV. WATER SAMPLE COLLECTION AND PRESERVATION

1. BOTTLES AND PRESERVATION

Surface water, soil or sludge samples for submittal to the DWR Chemistry Laboratory (the Lab) must be collected using Lab and EPA approved containers, and in accordance with approved collection, preservation and holding times. The Lab maintains a website with links to the approved preservation and holding times for all parameters for which the laboratory analyzes: http://portal.ncdenr.org/c/document_library/get_file?uuid=719b475c-c4a7-44c7-86a7-1804bbd432c9&groupId=38364. Field staff are responsible for being familiar with the Lab's procedures and following them accordingly. Preservatives can be added by pipette or pre-measured vials depending on the sensitivity of parameter being measured. If a parameter is not on the Lab's website, speak with the appropriate lab staff to determine how to proceed. Any samples submitted to the Lab must be accompanied by a Lab Sheet (Chapter 2-Figure 6). Immediately after sampling, labeling, and chemical preservation, samples are placed in coolers on ice, along with a temperature blank. Once samples arrive at the laboratory, support staff check the temperature blank (included in each cooler) to ensure that they are in appropriate temperature range (4 $\pm$ 2ºC), assign lab tracking numbers, and distribute them to the appropriate analytical units. Any samples not meeting temperature, holding time, or preservation requirements or are otherwise not submitted in accordance with the SOP are subject to rejection as per Section 13: *Corrective Actions* of the Laboratory Section QAM. Laboratory staff will attempt to contact collector by phone or email before rejecting. If conditionally accepted, the laboratory will document the anomaly with a Sample Condition Upon Receipt (SCUR) and/or Sample Anomaly Report (SAR) form and include copies with the final analytical report. Results from anomalous samples will be reported using the appropriate qualification code(s).

2. COLLECTION METHODS FOR CONVENTIONAL PARAMETERS

Collection for majority of the conventional parameters can be done by the multiple methods introduced in Chapter 1, "Sample Collection Types". The following section is an overview of the types of parameters collected by DWR along with the required sample size, bottle type, preservative method and holding time.

Note: There are some parameters that can ONLY be collected as a surface grab at 0.15 m below the surface and will be stated in the collection method statement. Although, holding times vary from hours to days, **all samples collected should be submitted to the laboratory as soon as possible.**

2.1. BOD 5 – Day (Biochemical Oxygen Demand) - This test determines the amount of organic material in wastewater and surface waters by measuring the oxygen consumed by microorganisms in decomposing organic constituents. The test consists of the determination of dissolved oxygen prior to and following 5-day incubation of the sample at 20°C, thus establishing the amount of oxygen used.

2.1.1 *Collection method*:

a. Collect sample in a 1-liter plastic bottle.
b. Deliver within 48 hours
c. Cool to 4°C
d. For WWTP effluents, collect the sample ahead of disinfection when possible.

2.2. COD (Chemical Oxygen Demand) - measures pollution strength (Sawyer & McCarty, 1967). It is a measure of the amount of oxygen required to oxidize organic and oxidizable inorganic compounds in wastewater and surface waters.

2.2.1 *Collection method:*

a. Collect sample in a 200 ml plastic bottle
b. Acidified the sample with H_2SO_4 to pH <2.
c. Cool the sample to 4°C
d. There is a 28 day holding period.

2.3. Coliform - Fecal coliform bacteria are superior to total coliforms as indicators of possible pathogenic contamination of water. The total coliform group includes organisms, principally of the aerogenes group, that are not necessarily of fecal origin. The aerogenes may be a considerable portion of the total coliforms on occasion. They may have no sanitary significance since they can come from soils and vegetation especially grains. Essentially all fecal coliforms, on the other hand, are of fecal origin and therefore potentially are accompanied by pathogens.

2.3.1. *General Collection Methods*

a. Collect sample with a 250 ml wide-mouth sterile plastic bottle supplied by the DWR Laboratory. These bottles must contain sodium thiosulfate and EDTA reagents.
b. Coliform sample is always collected as a surface grab sample. In no case should composite samples be collected for microbiological examination.
c. Do not rinse bottle with sample, but fill it directly to within 1-2 inches from the top to allow mixing of the sample before analysis.
d. Use caution to avoid contaminating the sample with fingers, gloves, or other materials.
e. Cool to 4°C and return to lab **in less than 6 hours** from time of collection. The DWR Lab will analyze any coliform samples that are received in less than 24 hours; however, the data may not be acceptable for some uses due to extended holding time.

2.3.2. *Surface Sampling By-Hand*

a. Grab sample should be collected directly into the sample bottle.
b. Remove the bottle top to protect bottle and cap from contamination; avoid touching the inside of the bottle and cap.
c. Grasp the bottle securely near the base with one hand and plunge the bottle mouth down into the water to avoid surface scum. Position the bottle towards the current flow and away from the hand of the collector, the shore, the side of the sampling platform, or boat. The sampling depth should be 0.15m below the water surface.
d. If the water body is static, create an artificial current by moving the bottle away from the sampler while tipping the bottle slightly to allow water to enter.
e. Tip the bottle slightly upwards to allow air to exit and the bottle. Fill the bottle to within 1-2 inches of the top.
f. After removal of the bottle from the stream, tightly stopper and label the bottle.

2.3.3. *Surface Sampling by Weighted/Cage Bottle Frame* (Figure 4, pg. 19)

a. Remove the cover and lower the device to the water.
b. It is preferable to use nylon rope which does not absorb water and will not rot.
c. Swing the sampling device downstream and then allow it to drop into the water while pulling on the rope so as to direct the bottle upstream.
d. Pull the sample device rapidly upstream and out of the water, simulating the scooping motion of grab sampling.
e. Take care not to dislodge dirt or other material from the sampling platform.

2.4. Residue (Solids) - Residue refers to solid matter suspended or dissolved in water or wastewater.

2.4.1. *Residue Types*

a. Total Residue - is the term applied to the material left after evaporation of a water sample, and its subsequent drying in an oven at a defined temperature. Total residue includes nonfilterable residue and filterable residue. Also known as Total Solids.
b. Nonfilterable Residue (Suspended) - the portion of total residue retained by a filter. The concentration of other water quality parameters is related to suspended solids since the

solid structure may contain biochemical and chemical oxygen demand materials, trace metals, nutrients, pesticides, and toxic or hazardous materials absorbed on the surface. Also, known as Total Suspended Solids.

c. Filterable Residue (Dissolved) - the portion of total residue that passes through the filter. Dissolved solids consist mainly of inorganic salts, small amounts of organic matter, and dissolved gasses. Also called Total Dissolved Solids.

d. Volatile and Fixed Residue - the residue remaining after ignition for 1 hour at 550°C represents the ash or fixed solids, and the weight loss incurred is a reasonably accurate measure of organic matter or volatile solids.

2.4.2. *Collection method*: Use a 500 ml plastic bottle to collect **each** type of residue sample and cool to 4°C. The sample has a holding time of 7 days.

2.5. Alkalinity/Acidity - Alkalinity is a measure of the buffering capacity of water - the power of the water to neutralize hydrogen ions - and it is expressed in terms of an equivalent amount of calcium carbonate. Alkalinity is caused by the presence of carbonates, bicarbonates, and hydroxides. Acidity is the power of the water to neutralize hydroxy ions - and it is expressed in terms of an equivalent amount of calcium carbonate. Acidity is a result of the presence of free carbon dioxide, strong mineral acids, weakly dissociated acids, salts of strong acids, and weak bases.

2.5.1 *Collection method:* Collect sample with a 200 ml (for each parameter) plastic bottle, cool to 4°C. Holding time is 14 days.

2.6. TOC (Total Organic Carbon) - Measures the organic carbon present in water. When an empirical relationship can be established between TOC, BOD, and COD, the TOC provides a quick and convenient way of estimating the other parameters that express the degree of organic contamination.

2.6.1 *Collection method:* Collect sample with a 200 ml plastic bottle, add H_3PO_4 to pH <2 and cool to 4°C. Holding time is 28 days.

2.7. Turbidity (Clarity of Water) – measured in Nephelometric Turbidity Units (NTU). Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines. Turbidity in waters is a result of suspended matter such as clay, silt, finely divided organic and inorganic matter, soluble colored organic compounds, and plankton and other microscopic organisms.

2.7.1 *Collection method*: Collect sample in a 200 ml plastic bottle, cool to 4°C. The sample should be protected from light. The sample must be received by the lab in **less than 48 hours**.

2.8. Chloride - Chlorides are found in most natural waters. They may be of natural mineral origin or artificially introduced. Chloride concentrations are higher in wastewater than in raw water because sodium chloride (NaCl) is

a common article of diet and passes unchanged through the digestive system (American Public Health Association, 1992). Industrial processes also increase chlorides in wastewater effluents.

2.8.1. *Collection method:* Collect sample in a 500 ml plastic bottle, typically collected directly from the water body as a surface grab (0.15m deep). Cool to 4°C. Holding time is 28 days.

2.9. Chlorophyll *a* and Algal Biomass

2.9.1. *Chlorophyll a* - Chlorophyll *a* is the photosynthetic green, photosynthetic pigment contained in plants. The measurement of this pigment provides an estimate of algal biomass.

Collection method: Use a 500 ml wide-mouth opaque plastic bottle to collect the sample. Cool to 4°C. Sample **must** be received by the laboratory in **less than 24 hours**.

2.9.2. *Algae* - Algae are used as biological indicators of water quality. By determining the types and quantity of algae present in a water body and utilizing physical and chemical data collected at the same time, inferences can be made concerning the trophic state of a water body. Algae are sampled from the water column (phytoplankton), attached to rocks and debris (periphyton), and from floating mats (filamentous/nuisance growths). The primary type sampled by DWR is phytoplankton, although all forms of algae can be sent to the Ecosystems Branch Laboratory of the Environmental Sciences Section for analyses.

Collection method: Samples for phytoplankton should be taken with an integrated depth sampling device (Labline water sampler).

a) This device should be lowered to twice the secchi depth (approximately 1% light penetration) and slowly raised to the surface.

b) Pour sample into a 500 ml plastic disposable bottle and preserve with approximately 2.5ml of modified Lugol's solution or until a dark straw color is reached.

c) If a Labline is unavailable, a surface grab sample can be taken.

d) Scoop samples are taken only when no quantitative methods are possible or as an additional sample for ease in identification. Live samples are taken as above (Labline preferred) but are not preserved. Cool to 4°C. Send to the Lab or EU lab in **less than 24 hours**.

2.9.3. *Chlorophyll a and Algal Sample Submittal Procedure*

a. Samples should then be sent to the Central Laboratory along with nutrient and chemical samples.

IV. WATER SAMPLE COLLECTION AND PRESERVATION

b. Bloom samples should include one preserved and one unpreserved (live) phytoplankton sample along with chlorophyll *a* and nutrient samples and a completed bloom form. Bloom forms and modified Lugol's solution (for preservation) are obtained from the Ecosystems Branch in Raleigh.

c. After samples are logged in at the Central Lab and with the Ecosystems Group, they are analyzed per the Ecosystems Branch's SOP manual.

2.9.4. *Parameters collected in conjunction with phytoplankton samples.*

a. Physical Parameters- Are measured at the surface and at every meter or half meter from the surface to bottom according to depth. Parameters include:

1. Temperature
2. Dissolved Oxygen
3. pH
4. Secchi Depth
5. Conductivity
6. Salinity should be taken where appropriate.

b. Chemical samples- Include ammonia/ammonium, nitrate/nitrite, total Kjeldahl nitrogen, orthophosphate, total phosphorous, and chlorophyll *a* are required to accompany phytoplankton samples.

NOTE: Check with the lab prior to sampling for orthophosphate to ensure analysis capabilities.

c. Map showing the location of the sampling site and/ or GPS coordinates.

2.10. Color - Color in water may result from the presence of natural metallic ions (iron and manganese), humus and peat materials, plankton, weeds, and industrial wastes. True color is the color of water from which turbidity has been removed by filtration or centrifugation. The term apparent color includes not only color due to substances in solution, but also that due to suspended matter. Apparent color is determined on the original sample without filtration or centrifugation. In stream samples, unaffected by industrial wastes, usually only true color is analyzed. In some highly colored industrial wastewaters, color is contributed principally by colloidal or suspended material. Therefore, apparent color may be a more appropriate measure for samples related to industrial wastewaters.

The color value of water is extremely pH dependent and increases as the pH of the water is raised. Therefore, always measure in-*situ* pH and specify the pH at which the color is determined.

2.10.1. *Accepted Methods to Determine Color*

There are three accepted methods to determine color (USEPA, 1994): Platinum-cobalt, spectrophotometric and ADMI. Each of these methods yields different information. Their proper uses and interpretations must be reviewed to determine the appropriate test based on the purpose of the sampling.

2.10.2 *Collection method:* Use a 200 ml plastic bottle to collect a surface grab sample. Cool sample to 4°C. Sample must be submitted to the lab in **less than 48 hours**.

2.11. Chromium, Hexavalent [Cr^{+6}] - The principal chromium emissions into surface waters are from metal-finishing processes such as electroplating, pickling, and bright dipping. Uncontrolled emissions have great potential for contaminating the fresh waters with the relatively toxic form, Cr (+6). Other smaller discharges of Cr^{+6} are from the additive in circulating cooling waters, laundry chemicals, and animal glue manufacture.

2.11.1 *Collection method*: Collect sample in a 200 ml plastic disposable bottle and cool to 4°C. Sample must be submitted to the lab in **less than 24 hours**.

NOTE : Lab should be notified that this sample will be submitted for analysis prior to sample collection.

2.12. Cyanide (CN^-) - Cyanides occur in the effluents from gas works and coke ovens, from the scrubbing of gases at steel plants, from metal cleaning and electroplating processes, and from chemical industries. Most of the cyanide in water is in the form of HCN (hydrogen cyanide). Toxicities may vary markedly with pH and a given concentration that is innocuous at pH 8 may become detrimental if the pH is lowered to 6 or less. In natural streams, cyanides deteriorate or are decomposed by bacterial action, so that excessive concentrations may be expected to diminish with time.

2.12.1 *Collection method:*

a. Use two 1 liter plastic bottles collect a surface grab sample directly from the water body.
b. Add NaOH to pH>12 and 0.6g of ascorbic acid if sample contains residual chlorine.
c. Cool sample to 4°C.
d. Sample has a holding time of 14 days.

2.13. Fluoride (F^-) - Fluoride at 0.8 to 1.5 mg/l in drinking water aids in the reduction of dental decay, especially among children. Fluorides in high concentrations are not a common constituent of natural surface waters, but they may occur in detrimental concentrations in ground water. Fluorides are used as insecticides, for disinfecting brewery apparatus, as a flux in the manufacture of steel, for preserving wood and mucilage, for the manufacture of glass and enamels, in chemical industries, and water treatment. While not normally found in industrial wastes, they may be present in traces, or in higher concentrations resulting from spillage.

2.13.1 *Collection method*:

a. Use a 500 ml plastic bottle to collect a surface grab sample directly from the water body.
b. Sample must be cooled to 4°C.
c. Holding time is 28 days.

2.14. Formaldehyde - (HCHO) formaldehyde is a colorless gas with a pungent odor. It is usually stored and transported as an aqueous solution containing 37-50% formaldehyde by weight and 1-15% methanol. Formaldehyde is used in the production of urea-formaldehyde and phenol-formaldehyde resins. These resins are used in the production of plywood, particleboard, foam insulation, and a wide variety of molded or extruded plastic items. Formaldehyde is intensely irritating to mucous membranes and the National Institute for Occupational Safety and Health recommends that formaldehyde be handled as a potential occupational carcinogen. Formaldehyde is used for preserving biological specimens.

2.14.1 *Collection method*:

a. Collect surface grab sample in a 500 ml disposable plastic bottle
b. Sample must be cooled to 4°C.
c. Although no holding time is specified for this sample, it should be submitted to the lab as soon as possible.

2.15. HEM: Grease and Oil - For the grease and oil analysis; groups of substances with similar physical characteristics are determined quantitatively on the basis of their common solubility in trichlorotrifluoroethane (Freon). Grease and oils, either vegetable oil and animal fats or mineral hydrocarbons, when introduced to surface waters, are found floating on the surface, emulsified or solubilized in the water column, or settled on the bottom as a sludge. Potential contributors to oil pollution are all agencies engaged in productions, transportation, handling, and use of oil. Also, ships, railroads, civic dumps, salvage dumps, machining operations, and the most notable - garages and filling stations. Grease from animal and vegetable oils enters waterways from food processors and restaurants. Surface waters are at all times to be kept virtually free from oil or grease, not only for esthetic reasons and taste and odor problems for domestic water supply, but evidence has demonstrated both acute lethal toxicity and long term sublethal toxicity of oils to aquatic organisms.

2.15.1 *Collection method:*

a. Collect 2 liters (two 1 liter glass wide mouth mason jars, Teflon-lined caps) of sample.
b. A surface grab sample at 0.15 m deep is the only collection method.
c. Acidify the sample with HCL or H_2SO_4 to pH <2.
d. Sample must be cooled to 4°C Holding time for this sample is 28 days.

IV. WATER SAMPLE COLLECTION AND PRESERVATION

2.16. Total Hardness - Hard waters are generally considered to be those waters that require considerable amounts of soap to produce a foam or lather and that also produce scale in hot water pipes, heaters, boilers, and other units in which the temperature of water is increased materially. In general, surface waters are softer than ground waters. The hardness of water reflects the nature of the geological formations with which it has been in contact. Natural sources of hardness principally are limestone that are dissolved by percolating rainwater made acid by dissolved carbon dioxide. Industrial and industrially related sources include the inorganic chemical industry and discharges from operating and abandoned mines.

Classification of water by hardness content (Conc., mg/l $CaCO_3$) (USEPA, 1976).

Soft	0 - 75
Moderately Hard	75 - 150
Hard	150 - 300
Very Hard	300 and Up

The constituents that impart hardness to water are polyvalent cations, chiefly calcium (Ca^{++}) and magnesium (Mg++). These form insoluble complexes with a variety of anions ($HCO3^-$, $SO4^-$, Cl^-, NO_3^-, SiO_3^-). By convention, hardness is reported on the basis of equivalence as mg/l calcium carbonate ($CaCO_3$).

The DWR Lab is no longer analyzing samples for Total Hardness, therefore, when a total hardness sample is required, a nitric acid (HNO_3)-preserved sample must be submitted for Ca and Mg (see section 2.23). Once the Ca and Mg results are received from the lab, total hardness is calculated using the following formula:

Total Hardness, mg/L = 2.497[Ca, mg/L] + 4.118[Mg, mg/L]

2.16.1. *Collection method:*

a. Sample must be collected as a surface grab (0.15 m from the surface) in a 500 ml plastic bottle.
b. Acidify the sample with HNO_3 to pH <2 and cool to 4°C.
c. Holding time is 6 months.

2.17. Specific conductance (Specific Electrical Conductance) - The specific conductance (conductivity) of a solution is a measure of its ability to carry an electrical current. This ability depends on the presence of ions, their total concentration, mobility, valence, and relative concentrations, and on the temperature of measurement. Specific conductance is the conductance afforded by 1 cc (ml) of a solution of electrolyte and is reported in micromhos per centimeter (µmhos/cm). Specific conductance measurements are used in water analysis to obtain a rapid estimate of the dissolved solids content of a water sample. This measurement is normally

made using a field meter; however, the following procedure can be used if necessary.

2.17.1. *Collection method*:

a. Use a 200 ml plastic bottle collected as a surface grab (0.15 m from the surface).
b. Sample should be cooled to 4°C.
c. Holding time is 28 days.

2.18 MBAS - Methylene-Blue-Active Substances - This test determines surfactants with no specificity, so the materials determined are designated as MBAS. This method depends on the formation of a blue salt or ion pair when methylene blue, a cationic dye, reacts with anionic surfactants. Surfactants are organic materials, which have the property of being surface active in aqueous solution. All surfactants have rather large polar molecules. One end of the molecule is particularly soluble in water and the other is readily soluble in oils. The surfactants include soaps, detergents, emulsifiers, wetting agents, and penetrants. Of these substances, the synthetic detergents are most important and are used in the greatest amounts. Presently, about 80 percent of all synthetic detergents are of the anionic type, and the MBAS method determines the presence of these surfactants. The most widely used anionic surfactant is linear alkylbenzene sulfonate (LAS). The detergent manufacturing industry changed to the production of LAS because it is more readily biodegradable than the older ABS (alkyl benzene sulfonates).

2.18.1 *Collection method*:

a. **The lab must be notified that this sample will be collected and submitted for analy**sis.
b. Use a 500 ml plastic bottle to collect a surface grab sample (0.15 m from the surface).and cool to 4°C.
c. Sample must be returned to the lab in **less than 48 hours**.

2.19. Phenols (C_6H_5OH) - An aromatic compound known as carbolic acid. In concentrated solution, phenol is quite toxic to bacteria and is widely used as a germicide. Phenol is obtained from coal tar and manufactured synthetically. It is used extensively in the synthesis of organic products, particularly phenolic-type resins. Phenolic wastes arise from the distillation of wood, from gas works, coke ovens, oil refineries, chemical plants, and from human and animal refuse.

2.19.1. *Collection method*:

a. Use two- 1 liter glass (phenol bottles) bottles to collect a surface grab (0.15 m from the surface)
b. Acidified the sample with H_2SO_4 to pH <2.
c. Cool the sample to 4°C
d. There is a 28 day holding period.

IV. WATER SAMPLE COLLECTION AND PRESERVATION

2.20. Sulfate (SO_4) - The sulfate ion is one of the major anions occurring in natural waters. Sulfates occur as the final oxidized state of sulfides, sulfites, and thiosulfates. Sulfates may also occur as the oxidized stage of organic matter in the sulfur cycle. Sulfates may be discharged in numerous industrial wastes, tanneries, sulfate-pulp mills, textile mills, and other plants that use sulfates or sulfuric acid. Sulfate is important to public water supplies because of its cathartic effect upon humans when it is present in excessive amounts (upper limit-250 mg/l U.S.P.H.S.). Sulfates are of considerable concern to wastewater treatment plants because of odor and sewer corrosion problems resulting from the reduction of sulfates to hydrogen sulfide (H_2S or hydrosulfuric acid in an aqueous solution).

2.20.1. *Collection method*:

a. Sample should only be collected as a surface grab sample.
b. Collect a surface grab (0.15 m from the surface) in a 500 ml plastic bottle
c. Cool the sample to 4°C.
d. Sample has a hold time of 28 days

2.21. Sulfide (S^-) - Sulfides are constituents of many industrial wastes tanneries, paper mills, chemical plants, and gas works. Sulfides are also generated in sewage and some natural waters by the anaerobic decomposition of organic matter. Sulfides react with hydrogen ions to form HS^- or H_2S. The toxicity of sulfides derives primarily from H_2S rather than from the hydrosulfide (HS^-) or sulfide (S^{-2}) ions. H_2S is very toxic and has claimed the lives of numerous workmen in sewers, but owing to the unpleasant taste and odor (rotten eggs), most persons or animals avoid consuming a harmful dose.

2.21.1. *Collection method:*

a. Samples should only be collect as a surface grab.
b. Collect three- 40 ml glass VOA vials with Teflon-lined septum directly as a surface grab (0.15 m from the surface)
c. Allow the sample to overflow the vial.
d. Add 0.1 ml of 2N zinc acetate plus 6N NaOH to pH >9.
e. cap the vial when sample is overflowing ,leaving no air space
f. Cool the sample to 4°
g. Holding time is 7 days.

2.22. Phosphorous and Nitrogen (Nutrients) - Phosphorus occurs in natural waters and in wastewater almost solely as phosphates. Evidence indicates that high phosphorus concentrations are associated with accelerated eutrophication of waters when other growth promoting factors are present, and aquatic plant problems develop in reservoirs and other standing waters at phosphorus values lower than those critical in flowing streams.

Nitrogen is one of the fertilizing elements essential to the growth of algae. Such growth is often stimulated to an undesirable extent in bodies of water that receive excess inputs of nitrogen from either point or nonpoint sources.

2.22.1 *Nutrient Types*

a. NH_3 (Ammonia) - In surface or ground waters, ammonia results from the decomposition of nitrogenous organic matter. It may also result from the discharge of industrial wastes from chemical or gas plants, from ice plants, or from scouring and cleaning operations where ammonia water is used. The conversion of ammonia to nitrites and nitrates by bacteria requires oxygen, and so the discharge of ammonia nitrogen and its subsequent oxidation can seriously reduce the dissolved oxygen levels in rivers and estuaries.

b. TKN (Total Kjeldahl Nitrogen) - Analytically, organic nitrogen and ammonia can be determined together and are referred to as Kjeldahl nitrogen, a term that reflects the technique used in their determination.

c. NO_2 + NO_3 (Nitrites + Nitrates) - Nitrites are quickly oxidized to nitrates. Nitrates are the end product of the aerobic stabilization of organic nitrogen. Nitrates also occur in percolating ground waters as a result of excessive application of fertilizer or leaching from septic tanks. Nitrates are seldom abundant in natural surface waters because of uptake by plants.

d. Total P (Phosphorus) - Phosphorus occurs in natural waters and in wastewater almost solely as phosphates. High phosphorus concentrations are associated with accelerated eutrophication of waters when other growth promoting factors are present.

e. PO_4 (Orthophosphate) - Orthophosphate is used as fertilizer and is applied to agricultural and residential cultivated land where it is carried into surface waters with storm runoff.

2.22.2 *Collection Methods for Unfiltered Nutrients* (NH_3, TKN, NO_2+NO_3, and Total P)

a. Use a 500 ml plastic disposable bottle for sample collected.
b. Acidify the sample with H_2SO_4 to pH<2 (to 500 ml sample add 2.0 ml 25% H_2SO_4 **Note**: Addition of an excessive amount of acid will interfere with the sample analysis
c. Cool the sample to 4°C.
d. Holding time is 28 days.

2.22.3. *Collection Method for PO_4 and Dissolved P (Filtered Nutrients)*

This water sample must be filtered in the field. A detailed Standard Operating Procedure for field filtering using a vacuum pump can be found in Appendix 6. Be careful- **do not** allow filter residue to touch filter apparatus or forceps.

a. Use a 200 ml plastic bottle for each sample.
b. **Dissolved P sample is acidized to pH <2 by adding 25% H_2SO_4.**
c. Dissolved P and PO_4 samples must be cooled to 4°C
d. **Holding time for PO_4 is less than 48 hours**
e. The holding time for Dissolved P is 28 days.

NOTE: For Turbid Samples - change filters during process.

2.23. METALS- The following metal parameters are collected in one bottle: Cd, Cr, Cu, Ni, Pb, Zn, Ag, Al, Be, Ca, Co, Fe, Li, Mg, Mn, Na, K, Ba, As, Se, Hg.

Whenever metal samples are collected the collection of field pH is essential. Metals are always collected as a surface grab

Collection method:

a. Collect 500 ml of sample in a plastic disposable bottle directly from the water body as a surface grab (0.15 from the surface).
b. Add HNO_3 to pH <2.
c. Cool the sample to 4°C.
d. Metals have a 6 month holding time with the exception of Mercury (Hg) which is 28 days.

2.23.1. *Cadmium (Cd)* - In the elemental form, cadmium is insoluble in water. It occurs in nature largely as the sulfide salt, greenockite or cadmium blend, often as an impurity in zinc-lead ores. Cadmium is used in metallurgy to alloy with copper, lead, silver, aluminum, and nickel. It is also used in electroplating, ceramics, pigmentation, photography, and nuclear reactors. Cadmium salts are sometimes employed as insecticides and antihelminthics. Cadmium salts may be found in wastes from electroplating plants, pigment works, textile printing, lead mines, and chemical industries. Cadmium has been shown to be toxic to man when ingested or inhaled.

2.23.2. *Chromium (Total Cr)* - The principal chromium emissions into surface waters are from metal finishing processes such as electroplating, pickling, and bright dipping. Other smaller discharges of chromium are from the additive in circulating cooling waters, laundry chemicals and animal glue manufacture, leather tanning, and textile dyeing. Chromium is one of the least toxic of the trace elements. Chromium is not acutely toxic to humans.

2.23.3. *Copper (Cu)* - Copper salts in natural waters are generally the result of pollution attributable to the corrosive action of water on copper and brass tubing, to industrial effluents, and algaecide. Copper salts are used in textile processes, pigmentation, tanning, photography, engraving, electroplating, insecticides, and fungicides. Because copper in concentrations high enough to be dangerous to human beings renders water disagreeable to taste, it is believed that copper is probably not a hazard in domestic water supplies. However, copper in water may be disadvantageous or detrimental for certain industrial uses. In trace amounts, copper may be beneficial or even essential for the growth of living organisms. In excessive quantities it has been found toxic to a wide variety of aquatic forms, from bacteria to fish.

2.23.4. *Nickel (Ni)* - Nickel toxicity to man is believed to be very low. Systemic poisoning of human beings by nickel or nickel salts is almost unknown. Nickel does not merit serious consideration as a water pollutant, but nickel ions may be detrimental to beneficial uses. Nickel is toxic to some plants. Nickel is used in metal plating, batteries, as a catalyst in the preparation of edible oils, and in solar energy equipment.

2.23.5. *Lead (Pb)* - Lead is a cumulative poison. The poisoning usually results from the cumulative toxic effects of lead after continuous, long-term consumption rather than from occasional small doses. Lead exists in nature mainly as the sulfide (galena). Some natural waters contain lead in solution where mountain limestone and galena are found. Lead may also be introduced into water as a constituent of various industrial and mining effluents or as a result of the action of the water on lead in pipes. Atmospheric fallout and rainout of particulate lead are considered the most significant sources of lead input into natural surface waters, especially in urban areas. Storm runoff originating in urban areas will tend to be high in lead concentration. The low solubility of lead in the aqueous phase of natural systems and the formation of stable complexes with organic matter are manifested in the low uptake by some plants and animals. There are extremely low concentrations of lead in natural bodies of water in proportion to the concentration in the beds of lakes and streams. The net effect of these sluggish dynamics is a high degree of accumulation with prolonged exposure.

IV. WATER SAMPLE COLLECTION AND PRESERVATION

2.23.6. *Zinc (Zn)* - Zinc is used extensively for galvanizing, in alloys, for electrical purposes, in printing plates, for dye manufacture, and dyeing processes. Zinc salts are used in paint pigments, cosmetics, pharmaceutics, dyes, and insecticides. Zinc is found in high concentrations in natural waters in zinc mining areas and in effluents from metal plating works. In most surface and ground waters it is present only in trace amounts. There is some evidence that zinc ions are absorbed strongly and permanently on silt with a resultant inactivation of the zinc. Zinc has no known adverse physiological effects upon man except at very high concentrations. For esthetic considerations, high concentrations of zinc in domestic water are undesirable. At 30 mg/l, zinc gives water a milky appearance and causes a greasy film on boiling. It is toward fish and aquatic organisms that zinc exhibits its greatest toxicity at much lower concentrations.

2.23.7. *Silver (Ag)* - Silver metal is used in jewelry and silverware, in alloys, for electroplating, and in the processing of food and beverages. Silver nitrate is used in photography, ink manufacture, electroplating, coloring porcelain, and as an antiseptic. Traces of silver can be expected to reach natural waters from such sources. Silver is bactericidal and toxic at low concentrations.

2.23.8. *Aluminum (Al)* - Aluminum is the third most abundant element of the earth's crust. Aluminum occurs in many rocks and ores and clays, but never as a pure metal in nature. The metal itself is insoluble, but many of its salts are readily soluble. Aluminum is not likely to occur for long in surface waters because it precipitates and settles, or is absorbed as aluminum hydroxide or aluminum carbonate. In streams the presence of aluminum ions may result from industrial wastes or more likely from wash water containing alum from water treatment plants.

2.23.9. *Beryllium (Be)* - A relatively rare element, found chiefly in the mineral beryl, this substance is not likely to occur in natural waters. Although the chloride and nitrate forms are very soluble in water and the sulfate form moderately so, the carbonate and hydroxide forms are almost insoluble in cold water. Beryllium is used primarily in metallurgy to produce special alloys, in the manufacture of X-ray diffraction tubes and electrodes for neon signs, and in nuclear reactors. Beryllium is not harmful when taken internally through the digestive tract but has been incriminated in pulmonary ailments of workers exposed to beryllium dusts.

IV. WATER SAMPLE COLLECTION AND PRESERVATION

2.23.10. *Calcium (Ca)* - Calcium is the most abundant dissolved cationic constituent of natural fresh waters. This element is widely distributed in the minerals of rocks and soils. Calcium carbonate is frequently found as a cementing agent between mineral particles of sandstone and other detrital rocks. Calcium is one of the constituents of hard water and is a scale former in hot water systems. Prevention of corrosion of cast iron water distribution systems may be obtained through controlled precipitation of calcium carbonate. Lime ($CaOH_2$), and dolomite [$CaMg(CO_3)_2$] are frequently employed as neutralizing agents in water and wastewater treatment.

2.23.11. *Cobalt (Co)* - Cobalt and its salts are used for making alloys, in nuclear technology, as pigment in the china and glass industry, and as binders in the tungsten-carbide tool industry. Cobalt has a relatively low toxicity to man, and traces of cobalt are essential to nutrition.

2.23.12. *Iron (Fe)* - Iron interferes with laundering operations, imparts objectionable stains to porcelain fixtures, and causes difficulties in distribution systems by supporting growths of iron bacteria. Iron also imparts a taste to water, which is detectable at very low concentrations. In addition to corrosion products, natural waters may be polluted by iron-bearing ground water.

2.23.13. *Lithium (Li)* - An alkali metal, it is not widely distributed in nature, being found in a few minerals and in certain spring waters. Lithium is used in metallurgy, medicinal waters, some types of glass, and, as lithium hydroxide, in storage batteries. Lithium is toxic at high concentrations.

2.23.14. *Magnesium (Mg)* - Magnesium ions are of particular importance in that they occur in significant concentration in natural waters, and along with calcium, form the bulk of the hardness reaction. Magnesium is considered relatively non-toxic to man and not a public health hazard because, before toxic concentrations are reached in water, the taste becomes quite unpleasant. At high concentrations, magnesium salts have a laxative effect, particularly upon new users, although the human body can develop a tolerance to magnesium over a period of time.

2.23.15. *Manganese (Mn)* - Manganese is essential for the nutrition of both plants and animals. Manganese is undesirable in domestic water supplies because it causes an unpleasant taste, deposits on food during cooking, stains, and discolors laundry and plumbing fixtures, and fosters the growth of some microorganisms in reservoirs, filters, and distribution systems. Manganese frequently appears in surface waters as the result of decaying vegetation, in waters with acid pH values, and acidic waters from coal mine drainage. In ground water subject to reducing conditions, manganese can be leached from the soil and occur in high concentrations.

IV. WATER SAMPLE COLLECTION AND PRESERVATION

2.23.16. *Sodium (Na*) - Sodium salts are extremely soluble in water; any sodium that is leached from soil or discharged to streams by industrial wastes will remain in solution. Sodium is the cation of many salts used in industry and as such is one of the most common ions in process wastes. Sodium in drinking water may be harmful to persons suffering from cardiac, renal, and circulatory diseases.

2.23.17. *Potassium (K)* - One of the more common elements, potassium is one of the most active metals, and for that reason it is not found free in nature but only in the ionized or molecular form. Potassium is used for fertilizers and some varieties of glass. It is an essential nutritional element, but in excessive quantities it acts as a cathartic.

2.23.18. *Barium (Ba)* - Barium ions are not normally present in natural surface or ground waters in measurable concentrations although they have been detected in a few springs and in effluents from areas where barytes, $BaSO_4$, or witherite, $BaCO_3$, are mined. Barium and its salts are used in the metallurgical industry for special alloys, in the paint industry, in cements designed to withstand salt water, and in the ceramic and glass industries. Because of possible toxic effects on the heart, blood vessels and nerves a surface water supply standard of 1.0 mg/l was established.

2.23.19. *Arsenic (As)* - Arsenic may occur in water as a result of mineral dissolution, industrial discharges, or the application of insecticides. Arsenic is toxic to humans and accumulates in the body.

2.23.20. *Selenium (Se)* - Elemental selenium is practically nontoxic, but hydrogen selenide and other selenium compounds are extremely toxic and resemble arsenic in their physiological reactions. Selenium poisoning occurs mostly among livestock, and the toxic effects appear to be associated with the consumption of high concentrations of selenium in food, such as locoweed or grains grown in soils with high concentrations of selenium, rather than from water consumption. Selenium occurs in sulfur deposits, sulfides of metals, volcanic emissions, sedimentary rocks, organic-rich soils, and coal. Selenium is used in the electronics industry, xerographic copying machines, photoelectric cells, glass and ceramics, pigment manufacture to color plastics, paints, enamels, inks, and rubber. It is also used as a component of plating solutions. It can also be found in discharges from coal-fired power plants.

2.23.21. *Mercury (Hg)* - Mercury and mercuric salts are considered to be highly toxic to humans and aquatic life. Elemental mercury is inert chemically and insoluble in water, and is not likely to occur as a water pollutant. Mercuric salts occur in nature chiefly as the sulfide HgS, known as cinnabar, but numerous synthetic organic and inorganic salts of mercury are used commercially and industrially. They are used in medicinal products, disinfectants, detonators,

pigments, and photoengraving. Many of the mercuric and mercurous salts are highly soluble in water.

3. PESTICIDES AND ORGANICS

3.1. Pesticides - Pesticides are any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating insects, rodents, fungi, viruses, or weeds, and other forms of plant or animal life considered to be pests. Pesticides are categorized into three groups:

- Inorganic - arsenicals, mercurials, borates, and fluorides
- Synthetic organic - chlorinated hydrocarbons, organic phosphates, and thiocarbamates
- Natural organic - rotenone, pyrethrum, and nicotine

Pesticides may also be classified by their biological usefulness as algaecides, acaricides, fungicides, and herbicides.

3.2. Organics - All organic compounds contain carbon in combination with one or more elements.

3.3. Collection Methods

3.3.1. *Pesticides, semivolatile organics, and acid herbicides*

a. Collect each sample (Pesticides, semivolatile organic & acid herbicides) into a separate 1 gallon amber glass jug with a Teflon-lined cap.
b. The sample is collected directly from the water body as a surface grab (0.15m deep).
c. Add sodium thiosulfate and cool to 4°C.
d. Holding time is 7 days.

3.3.2. *Purgeable Organics (VOA)*

a. Collect sample into three-40 ml Teflon vials, remove cap underwater.
b. When collecting in waters with no chlorine, use vials pre-preserved by the Central Laboratory with sodium bisulfate ($NaHSO_4$).
c. The vial should be filled and capped underwater (0.15m deep) with no air space in the vial. While keeping lid and bottle under water gently rock the lid and bottle to remove air bubbles (unless bottle is pre-preserved). The volatile organics vials should be completely filled to prevent volatilization, and extreme caution should be exercised when filling a vial to avoid any turbulence that could also produce volatilization.
d. When collecting in waters where chlorine is present, first preserve an empty vial with 0.6 g of ascorbic acid before filling and capping the vial underwater. After capping the vial, remove the vial above water, uncap, and add 0.25 g of sodium bisulfate leaving no air space before recapping the vial.

e. The three vials should be placed in a Ziploc bag in the cooler. A trip blank is also required. This is a vial filled at the laboratory with appropriate bottled water and placed in a Ziploc bag in the same cooler with the other VOA vials.
f. A separate laboratory sheet is filled out for the trip blank and this sample is used to determine if any contamination has occurred of the VOA samples.
h. Cool to 4°C.

3.3. Instructions for requesting a pesticide or organic analysis

When a particular pesticide or organic is suspected or known to be present in a sample, its name should be entered on the laboratory form. With this information, the laboratory can focus immediately on the analytical methodology for determining the presence and concentration of the suspected pollutant and as a result possibly decrease the analysis time. A list of specific pesticides and organics currently analyzed at the Laboratory is available online: http://portal.ncdenr.org/web/wq/lab/ops/org

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V. SEDIMENT COLLECTION AND PRESERVATION

1. COLLECTING SUSPENDED SEDIMENT

1.1. Samplers and Applications

For more descriptive information about these samplers see references (Inter-Agency Committee on Water Resources 1965).

1.1.1. *U.S. DH-48 – When in wadable streams*

1.1.2. *U.S. DH-59 [Equal Width Increment Method (E.W.I.)]*

1.1.2.1 Used When

a. Too deep for wading but less than 15 feet deep.
b. From low bridges.
c. Velocities less than approximately 5 ft/ sec.

1.1.2.2 Sampling Tips

a. Set out safety equipment (cones, high visibility vests, etc.) as necessary and assemble sampling equipment. Note: Prior to using any sampler, it should be thoroughly cleaned and inspected.
b. Rinse sampler with distilled water before the first station and between stations to wash away any contaminants.
c. Use the upstream side of bridges if possible.
d. Go to midstream or the area where most of the flow is occurring. First sampling point must be made where the flow is greatest.
e. Lower and raise the sampler at a consistent rate with the nozzle oriented upstream to the bottom, immediately reverse it and raise to above the water surface. Repeat until jar is filled within approximately 3 inches of the top of the jar (350-440 cc). Rate must not exceed 0.4 times the mean velocity and must be fast enough to keep from overfilling.
f. If bottle overfills - discard sample, rinse bottle, and collect again. Use a smaller nozzle or a faster transit rate.
g. Raise the sampler and pour contents into a cleaned sample splitter. For cleaning instructions see USGS references. The sample splitter should be rinsed with distilled water before the first station and between stations.
h. Sample at the next sampling point and place contents into a mixing churn.

i. Ideally try for 3 sampling points, midstream and quarter points, but the situation might indicate otherwise (if maximum flow is not midstream). Sampling points should be equally spaced.
j. If more sample is needed for the churn, take a second set of samples at the same transit rate at all verticals.
k. Churn sample at a uniform rate of about nine inches per second. Disc should touch the bottom of the tank on every stroke and the stroke length should be as long as possible without breaking the water surface.
l. After churning for about l0 strokes, withdraw sub-samples and place in ½ liter bottles. As sub-samples are withdrawn, maintain churning rate. If there is a break in withdrawals, the stirring rate must be re-established before withdrawals can continue.

1.2. Variations on Suspended Sediment Sampling

1.2.1. When suspended materials in the stream are uniformly distributed, a representative sample can be obtained by sampling vertically at one location near the center of the flow.

1.2.2. Use surface or dip sampling instead of depth integrated sampling when:

- Stream velocity is too high.
- Large floating and moving submerged debris is in the stream.
- A depth-integrated sampler is not available.
- The depth of the stream is very shallow.

2. COLLECTING BOTTOM SEDIMENT

2.1. Containers and Volumes

2.1.1. *Sample Containers*

a. Use certified jars for sediment samples or as indicated by Chemistry Laboratory.
b. Use Teflon lid or parafilm between jar and lid for nutrients and all metals.
c. Tin foil can be used between jar and lid for all metals except aluminum.
d. Use Teflon lid or tinfoil for pesticides.

2.1.2 *Required volume*

- One pint of sample must be obtained for analyses of metals, nutrients, and organics.

3. BOTTOM SEDIMENT SAMPLERS, APPLICATIONS, AND PROCEDURES

For more descriptive information about these samplers see references.

3.1. Ekman grab (Figure 12)

3.1.1. *Locations Suitable for Use*:

a. Use in soft finely divided littoral bottoms of lakes, ponds, and streams that are free from vegetation (sticks, partially decayed leaves, etc.) as well as intermixtures of sand, stones, and other coarse debris.
b. Calm waters.
c. Low velocity streams.
d. Low bridges (messenger can damage spring mechanism if used from high bridges)

3.1.2. *Sampling Tips:*

a. Make sure grab is operating correctly. The grab can cause severe injury. Do not activate unit while holding.
b. If sampling from a low bridge, it may be advisable on wide streams to take 3 samples (midstream and quarter sections) and composite them to form l sample in a Nalgene mixing tub.
c. Set in open position by locking open the spring operated jaws.
d. Operating procedures are similar to those of the Petersen grab starting at step 5.2.6.

Figure 12. Ekman Grab Samplers

3.2. Petersen grab (Figure 13)

3.2.1. *Locations Suitable for Use:*

a. Hard bottoms (sand, gravel, marl, clay, etc.).
b. Strong velocities.
c. Very deep water

3.2.2. *Sampling Method and Tips*

a. Use with hoist because of its weight.
b. Make sure grab is operating correctly and rinse in water at first station and between stations.
c. Move jaws to open position, bring free end of horizontal locking bar into position in the locking notch on upper bar, insert safety pin lock.
d. Swing grab over side, remove safety pin lock, and lower slowly to bottom.
e. When grab is at the bottom, allow a moment for it to sink into the bottom then slack off on the line.
f. Resume tension on the line to close grab.
g. Pull grab to surface, swing inboard over a tub and discharge sample.
h. Place sample in jar. Approximately one pint of sample is needed.
i. If jaws of grab are jammed due to a stick, rock, or other hard object, discard sample, clean grab and sample again.

Figure 13. Peterson Grab Sampler

3.3. Ponar grab (Figure 14)

3.3.1. *Locations Suitable for Use:*

a. All types of bottoms except the hardest clays.
b. Strong velocities.
c. Very deep water

3.3.2. *Sampling Method and Tips*

a. Use with hoist because of its weight.
b. Make sure grab is operating correctly and rinse in water at first station and between stations.
c. Move jaws to open position, bring free end of the horizontal locking bar into position in locking notch on upper bar and insert safety pin lock.
d. Remove safety pin lock and lower sampler slowly.
e. When the grab is at the bottom, wait a minute to allow it to sink, and then slack off the cable.
f. Lift the sample maintaining tension and raise steadily and slowly to surface.
g. Swing inboard and open sampler over a tub to discharge sample.
h. Place sample in jar. Approximately one pint of sample is needed.
i. If an object is wedged between the jaws, discard sample, clean sampler, and sample again.
j. At the conclusion of sampling, replace the safety pin lock.

Figure 14. Ponar Grab Sampler

4. BOTTOM CORE SAMPLERS, APPLICATIONS, AND PROCEDURES

4.1. Phleger core sampler (Figure 15.)

4.1.1. *Locations Suitable for Use:*

a. Use with hoist because of its weight.
b. Use where water is too deep to use hand coring devices.
c. Sampling soft, sandy or semi-compacted sediments.

4.1.2. *Phleger Core Sampler Methods*

a. Make sure sampler and core tubes are clean and operating properly, rinse corer at first station and between stations.
b. Lower sampler to bottom, then raise off the bottom approximately one to two meters.
c. Drop sampler again to collect core.
d. Swing sampler inboard over a Nalgene tub.
e. Remove tube and core, measure out top two inches of core.
f. Place this portion of core into jar.
g. Repeat sampling until approximately one pint of sample is obtained.

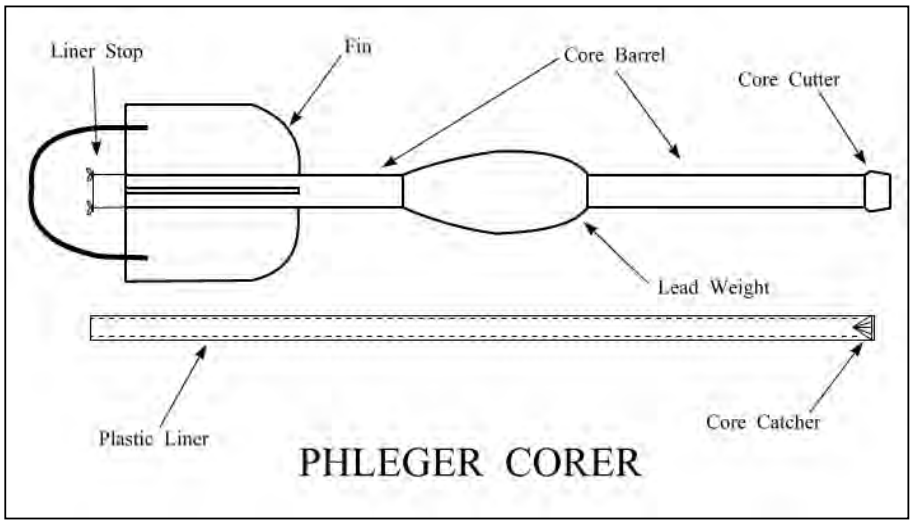


Figure 15. Phleger Corer Diagram

4.2. Wildco Light Duty Model 2414 Core Sampler

4.2.1. *Locations Suitable for Use:*

a. Use by hand or on the end of a line.
b. Where sediment is relatively soft.

4.2.2. *Wildco Light Duty Model 2414 Core Sampler Methods*

a. Make sure sampler and core tubes are clean and operating properly, rinse corer at first station and between stations.
b. Lower sampler to bottom, raise again and drop if necessary to take sample.
c. Remove plastic core, measure out top two inches of core.
d. Place this portion of core into jar.
e. Repeat sampling until approximately one pint of sample is obtained.

4.3. Hand coring device– for shallow water use.

4.3.1 *Procedure for hand coring device:*

a. Make sure sampler is clean before using. Rinse before first station and between stations.
b. Take sample by turning sampler into sediment.
c. Remove sampler and core.
d. Measure out top two inches of core.
e. Place this into jar.
f. Repeat sampling until approximately one pint of sample is obtained.

4.4. Hand Sampling Method

a. Face upstream in shallow, wadable streams.
b. Make sure that spoon or scoop has been thoroughly cleaned.
c. Scoop the sample directly into the jar and get a representative sample. It may be advisable to take several samples and consolidate (midstream and quarter points).

VI. STANDARD CLEANING PROCEDURES

1. GENERAL

The procedures outlined in this section are to be used by all personnel to clean sampling equipment and sample containers prior to field use. These procedures assure the standard operating procedures (SOP) for the Section; any deviation from them must be documented in field records and investigative reports.

All equipment and sample containers that are cleaned using these procedures will be tagged, labeled or marked with the following information:

- Name of person cleaning equipment or containers
- Date equipment or containers were cleaned
- Any deviation from SOP that was employed

All equipment and reusable sample containers used to collect samples will be identified at the conclusion of sampling activities. Any problems encountered with the equipment or needed repairs will also be noted. Equipment or reusable sample containers needing cleaning or repairs should not be stored with clean equipment, sample tubing or sample containers. Equipment, reusable sample containers, disposable sample containers, and sample tubing that are not used during the course of an investigation may not be replaced in storage without being re-cleaned if these materials are transported to a facility or study site where herbicides, pesticides, organic or other toxic materials are present or suspected of being present. All portions of unused coils of tubing that are returned shall be re-cleaned before being restocked. If these materials are transported to a facility in connection with a routine inspection or study where toxic or organic materials are not known or not suspected of being present, they may be placed back in storage without being cleaned.

Sufficiently clean equipment and sample containers should be transported to the field so that an entire study can be conducted without the need for cleaning equipment in the field. However, this will not always be possible when using coring equipment, dredges, buckets, water samplers, pumps and other such equipment. Field cleaning procedures are included to cover these special problems. Emergency field sample container cleaning procedures are also included; however, they should not be used unless absolutely necessary. Specific cleaning procedures are included in the following paragraphs.

2. AUTOMATIC SAMPLING EQUIPMENT

2.1. General Cleaning

2.1.1. *For All Automatic Samplers*

a. The exterior and accessible interior (excluding the waterproof timing mechanism) portions of automatic samplers will be washed with phosphate free laboratory detergent and rinsed with tap water.

b. The face of the timing case mechanism will be cleaned with a damp cloth.

c. All sample intake tubing will be discarded after use. Pump tubing should be cleaned with pesticide grade solvents.

d. New pre-cleaned, silicone pump tubing (see section on cleaning tubing) will be installed with the aluminum or Teflon tubing caps intact.

f. When using the samplers for collecting samples for metals and/or organic samples, the metal distributor tubes should not be used for this purpose.

g. The automatic samplers should not be used for collecting samples for organic analyses in the individual bottle mode since there is no way to properly clean the distributor plate to remove any residual organic compounds. The sample tubing headers may not be used to collect samples for organic analyses for the same reason.

2.2. ISCO Specific Cleaning Procedures

2.2.1. *Automatic sampler rotary funnel, distributor and metal tube*

a. Use only for non-organic sample collection using individual sequential bottles.

b. Clean with hot water, phosphate free laboratory detergent and a brush.

c. Rinse thoroughly with hot tap water.

d. Rinse thoroughly with distilled water.

e. Replace in sampler.

2.2.2. *Automatic sampler headers*

a. Rinse entire header with hot water, a bottle brush, and phosphate free laboratory detergent.

b. Disassemble header and rinse thoroughly with hot tap water, using a brush to remove particulate matter and surface films.

c. Rinse plastic portion of the header with 20 percent nitric acid. Do not use acid on metal parts.

d. Rinse thoroughly with tap water.

e. Reassemble header and rinse with distilled water.

f. Let dry thoroughly and wrap with aluminum foil.

g. Headers may not be used when collecting samples for organic analyses.

2.2.3. *Glass reusable composite containers (2 ½, 3 and 5 gallon capacities)*

a. After using, rinse with water in the field, seal with aluminum foil to keep the interior of the container wet and return to the laboratory.
b. Wash thoroughly with hot tap water and phosphate free laboratory detergent, using a bottle brush to remove particulate matter and surface film.
c. Rinse thoroughly with hot tap water.
d. Wash with 10 percent nitric acid.
e. Rinse thoroughly with tap water (at least 3 times).
f. Rinse thoroughly with distilled water (at least 3 times).
g. Rinse thoroughly with acetone (pesticide grade). Caution: Acetone must be removed before using. Residual acetone will interfere with certain analyses.
h. Rinse twice with distilled H_20. Allow to air dry,
i. Cap with aluminum foil or Teflon film.
j. Do not use composite containers used to collect samples at facilities manufacturing pesticides, herbicides or other toxic or noxious compounds. These are to be properly disposed of at the DWR Chemistry Laboratory.
k. Glass composite containers used to collect in-process wastewater samples at industrial facilities will be discarded after sampling.
l. Any bottles that have a visible film scale or discoloration remaining after this cleaning procedure are to be discarded.

2.2.4. *Glass sequential sample bottles (automatic sampler base for sequential mode)*

a. Rinse bottles in the field after using with tap water and seal with aluminum foil or cap for return to laboratory.
b. Rinse thoroughly with hot tap water.
c. Wash with 20 percent nitric acid.
d. Rinse thoroughly with tap water.
e. Place in dishwasher - phosphate free detergent cycle followed by tap and distilled water rinse cycles.
f. Replace in covered, automatic sampler base; cover with aluminum foil for storage.

2.2.5. *Bottle siphons*

a. Use a new siphon for each sampling location.
b. Pre-rinse the 3/8 inch Teflon tubing (used to make siphons for organic analyses) as in Teflon tubing cleaning instructions.

c. Flush the PVC 3/8 inch tubing used for samples other than those collected for organic analyses with sample before use.

2.2.6. *Teflon composite mixer rods*

- Use the sample cleaning procedure outlined for glass reusable composite containers above.

2.2.7. *Automatic sampler rubber pump tubing*

- Only new pre-rinsed tubing should be used for each automatic sampler set up

a. Rinse tubing with hot tap water for five minutes.
b. Rinse outside of tubing with hexane.
c. Install in automatic sampler.
d. Cap both ends of tubing with aluminum foil or Teflon film.

2.2.8. *Teflon sampler tubing (pure Teflon or Teflon lined)*

a. If required length is known pre-cut Teflon tubing or clean l00 feet coil intact.
b. Rinse outside of tubing with hexane.
c. Flush interior of tubing with hexane.
d. Air dry.
e. Cap each end of tubing with aluminum foil or Teflon tape and completely wrap the coil of Teflon tubing with aluminum foil to prevent contamination.

2.2.9. *Polyvinyl chloride sample (PVC) tubing (1/18, l/l4, or 3/8 Inch)*

a. Use only new tubing.
b. Use in selective sampling where organics are not of concern.
c. Flush the tube with sample immediately after the sampler is set up at the sampling site to remove any residues from the manufacturing or extruding process.
d. Store tubing in original container and do not removed from this container until needed.

2.2.10. *Stainless steel tubing*

Tubing will be flushed in the field with tap water after use and cleaned as follows upon return to the laboratory:

a. Wash with phosphate free laboratory detergent and a long bottle brush.
b. Rinse with hot water for 5 minutes.
c. Rinse with acetone.
d. Rinse with distilled water for one minute.
e. Air dry.
f. Rinse with hexane.
g. Completely wrap tubing, including ends, with aluminum foil to prevent contamination during storage.

3. MISCELLANEOUS SAMPLING AND FLOW MEASURING EQUIPMENT

Miscellaneous flow measuring and sampling equipment should be washed with phosphate free laboratory detergent and rinsed with hot tap water before being stored. For Lablines, rinse at least three times with distilled deionized water and cover the top of the Labline with foil to prevent contamination and to show that the Labline has been cleaned.

A different procedure is used for any equipment utilized in organic or toxics sampling.

4. STAINLESS STEEL SAMPLING EQUIPMENT

For collecting samples for organic analyses:

4.1. Follow the procedures given in the Automatic Sampler Section, Glass Reusable Composite Containers, but omit acid rinse.

4.2. Wrap equipment completely in aluminum foil to prevent contamination during storage.

5. OTHER FIELD INSTRUMENTATION

NOTE: Where available, always follow the manufacturer's recommendations for cleaning the device (see Appendices 1-4).

The exterior of sealed, watertight equipment such as Labline Samplers and field meters should be washed with a mild detergent (liquid dishwashing detergent, for example) and rinsed with tap water before storage. The interior of such equipment may be wiped with a damp cloth if necessary. Other field instrumentation should be wiped with a damp cloth. Probes for pH, conductivity, DO, etc. should be rinsed with distilled water before storage. The desiccant in flow meters and other equipment should be checked and replaced if necessary each time the equipment is cleaned.

Keep meters clean and in good operating condition. Probes should be rinsed at the end of each sampling day, properly stored and cleaned on a regular basis.

6. ICE CHESTS AND SHIPPING CONTAINERS

All ice chests and reusable shipping containers will be washed with a mild detergent (interior and exterior) and rinsed with tap water and air dried before storage.

7. FIELD CLEANING PROCEDURES

For routine operations involving classic parameter analyses, water quality sampling equipment such as Kemmerers, buckets, DO dunkers, dredges, etc. may be cleaned with sample or tap water between sampling locations. A brush may be used to remove deposits of material or sediment if necessary. Flow measuring equipment such as weirs, staff gages, velocity meters, and other stream gauging equipment should be cleaned with tap water after use and between measuring locations. When sampling equipment (not tubing) is to be utilized for collecting organic or toxic samples, the following cleaning procedure is to be used between sampling locations:

- Clean with tap water and brush if necessary.
- Rinse with pesticide grade acetone.
- Rinse thoroughly with tap water (if available).
- Rinse with distilled water.

It must be emphasized that these procedures are only to be used in the field. All equipment will be cleaned before storage at the laboratory utilizing the procedures previously outlined.

8. VEHICLES

All vehicles used by staff should be washed on a routine basis. This routine maintenance should minimize any chance of contamination of equipment or samples due to contamination of vehicles. When vehicles are used in conjunction with hazardous waste site inspections, or on studies where pesticides, herbicides, organic materials or other toxic matter are known or suspected to be present, a thorough interior and exterior cleaning is mandatory at the conclusion of such investigations. All vehicles shall be equipped with trash bags and/or trash containers to facilitate vehicle cleaning. All contaminated trash and equipment must be kept separate from ordinary trash and must be disposed of properly on-site or on return to the facility.

9. DISPOSABLE SAMPLE CONTAINERS

All disposable sample containers will be stored in their original packing containers in a clean, dust free environment. When any packing container is opened, all disposable sample containers inside should be immediately capped if they are found uncapped.

VII. TIME-OF-TRAVEL & DYE TRACING

1. FLUORESCENT DYE

The preferred dye for use in time-of travel studies by the North Carolina Division of Water Resources is Rhodamine W. T. (20%) solution. This is a red fluorescent dye which mixes well with water and is easily detected through visual means under high concentrations and through the use of a fluorometer for concentrations to as low as 0.01 parts per billion. Rhodamine WT has properties essential for water tracing studies. Rhodamine WT is:

- water soluble,
- highly detectable-strongly fluorescent,
- fluorescent in a part of the spectrum not common to materials generally found in water, thereby reducing the problem of background fluorescence,
- harmless in low concentrations,
- inexpensive, and
- reasonably stable in a normal water environment (Wilson, Cobb & Kilpatrick, 1986).

Rhodamine dye can also be used to determine such things as short-circuiting in wastewater treatment plants, outlets from storm drains, septic tank leakage, etc.

Most of ISB's dye studies are performed as part of a waste-load allocation model. This model requires that a stream be segmented into different reaches based upon predicted stream velocities, stream morphology, total distance of the study area, and major inputs from dischargers and tributaries. A dye sampling station is required in each of these reaches.

1.1. Safety

(MSDS is kept with dye container)

1.1.1. *Personal Protection*

a. Latex or vinyl gloves (in lab and field).
b. Goggles
c. Ventilated room
d. Apron

1.1.2. *Emergency and First Aid Procedure*

a. Inhalation:
- move to fresh air.
- Give oxygen and medical help if breathing is difficult.

b. Eye contact:
- Flush eyes with flowing water for at least 15 minutes, holding eyelids apart to irrigate thoroughly.
- Get medical attention right away.

c. Skin contact:
- Wash affected skin areas thoroughly with soap and water.
- If irritation develops, consult a physician.

d. Ingestion:
- If swallowed, dilute with water and induce vomiting.
- Get immediate medical attention.
- Never give fluids or induce vomiting if patient is unconscious or has convulsions.

1.2. Equipment - Fluorometer

1.2.1. Turner Designs Model 110 - reads dye concentrations directly in ppb. Operating instructions are contained in the Turner Designs Model 10 Operators manual, section 3-operations.

1.2.2. Turner Model 10-AU - reads dye concentrations in ppb. Operating instructions are contained in the Turner Designs Model 10-AU operating manual.

2. PRE-SURVEY

2.1. Surface Water Supplies

2.1.1. Identify all surface water supplies in or downstream from the study area.

2.1.2. Notify each water supply operator that may be affected in the study area, the DENR - Division of Water Resources regional water quality supervisor that a dye study is scheduled to be performed. Explain the reason for the study and inform the water treatment operator that DWR personnel will monitor dye concentrations at their water intake. If dye concentrations in the river exceed 10 ppb, the facility will be informed to shutdown their operation until river dye concentrations fall below 10 ppb. All efforts should be made to calculate a dye dosage that will result in a dye concentration at a water supply significantly below the 10 ppb.

2.2. Field Reconnaissance

1. Select dye sampling stations. Stations are selected based upon access, distance from the dose, and model requirements.
2. Locate all USGS gage stations in the study area or sites at which flows can be performed.
3. Determine if any dam structures that can regulate flow exist in the study area. If there is such a dam structure, a station is usually set up just upstream of the dam and an additional dose is made below the dam.

3. DYE REQUIREMENTS (ESTIMATING DOSAGE)

For Rhodamine WT 20 percent dye the dosage formula is:

$$V = 3.4 * 10^{-4} * [(Qm * L)/Vm]^{0.93} * Cp$$

Where:

V is the volume of dye, in liters
Qm is the maximum discharge in the reach, in cfs
L is the distance from injection to sampling point, in miles
Vm is the mean velocity, in fps
Cp is the peak concentrations desired in µg/l

The volume of Rhodamine WT 20 percent dye required to produce a peak concentration of 1 µg/l (ppb) can be determined from the nomograph in Figure 16 for a range of flow-reach conditions.

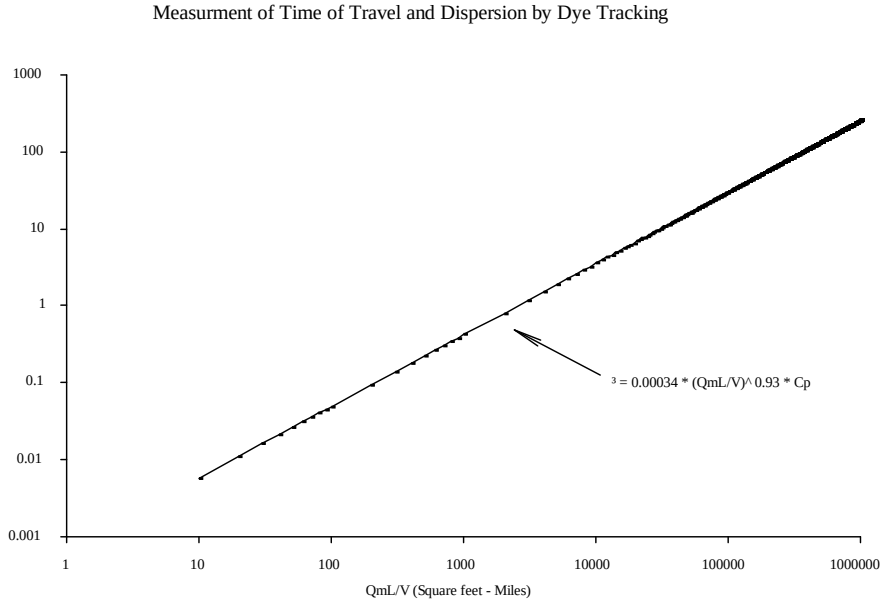


Figure 16. Nomograph for determining volume of dye necessary to produce peak concentration

4. INJECTION OF DYE

4.1. Injection Types

4.1.1. *Single Slug Injection*

a. A single slug injection of dye is usually made in the center of the thread of flow.
b. The desired quantity of dye as calculated in part 3 (above) can be poured into the stream from a container.

4.1.2. *Continuous injection*

a. The desired quantity of dye is pumped into the water column at a fixed rate for a fixed time using an ISCO sampler or a peristaltic pump. Tubing is run from the pump to the desired dye injection point. Contaminated pump lines are first flushed with stream water and then placed in plastic bags for shipment back to the lab.

5. COLLECTION OF WATER SAMPLES

Samples should be taken in pre-numbered glass bottles by a hand sampler or by ISCO samplers. Care should be taken to collect samples in the peak concentration of the dye cloud, i.e. do not sample midstream if the dye cloud is along one stream bank.

5.1. Dye Sample Collection

5.1.1. *Data recorded on field sheets* (Figure 17)

a. Station Location-Sampling Point
b. Date
c. Sample Bottle Number
d. Time
e. Name of Sampler

5.1.2. *Methods and Guidance*

a. At least one background sample is needed for measurement of background fluorescence at each site in the study reach before the dye arrives.
b. Sampling should begin early enough to determine the true dye peak.
c. Sampling should continue until a peak has been determined; and until a decreasing trend has been clearly established.

5.5.1. *Sampling Schedule*

a. The schedule for collecting samples at each sampling site is the most uncertain aspect of the plan.

b. Estimates of the time to begin sampling, time intervals between samples, and the duration of sampling must be made, which will ensure adequate definition of the dye cloud passing each site. It is better to start with more frequent sampling and decrease frequency based on sampling results when travel times are unknown.
c. An estimate of the time-of-travel between sampling sites is usually based on the cloud's movement to the first sampling site downstream of the injection site.

WATER QUALITY SECTION
INTENSIVE SURVEY
DYE TRACER STUDIES

SUB-BASIN: ___________

STREAM: ______________________________ LOCATION: __________________________________

SAMP. NO	SAMP Point	DATE	TIME	G. H. OR RP-WS	FIELD READINGS				LABORATORY READINGS				CONC (ppb)
					1X	3X	10X	30X	1X	3X	10X	30X	

COMMENTS:

Figure 17. Dye Tracer Study Field Sheet

5.6. Sample Collection Methods

5.6.1. *Hand Sampling*

a. Grab sample by hand dipping a bottle or by using a dye sampler.
b. Depth integrated sample a Labline sampler is needed.

5.6.2. *Automatic Samples (ISCO Sampler)*

a. Samples can be analyzed directly from the ISCO bottles, however, if the ISCO bottles are needed to continue sampling the samples can be transferred to numbered glass bottles.
b. Label bottle racks.
c. To reuse ISCO bottle, rinse three times using tap water or if tap water is unavailable uncontaminated stream water can be used.

6. FLUOROMETER USE

Refer to fluorometer manufacturer's operating instructions for specific procedures and service instructions. The Turner Designs Model 10 Fluorometer has two main scales; an X1 and an X100. When the fluorometer is in the X1 position, the sensitivity of the instrument is as indicated by the range lights. When the fluorometer is in the X100 position, the sensitivity of the instrument is 100 times that indicated by the range lights.

The scale for the Turner Designs Model 10 Fluorometer is:

Scale	Range	Concentration (ppb)
X100	X10	0-1
X100	minimum sensitivity	1-10
X1	X10	10-100
X1	minimum sensitivity	100-1000

6.1. Fluorometer Usage

6.1.1. *Calibration-*

(Fluorometric Procedures for Dye Tracing, Book 3, Chapter A12, Revised 1986.)

a. Use a range of dye concentrations (ex. 1 µg/l, 10 µg/l, 50 µg/l, 100 µg/l with µg/l=ppb) to calibrate the fluorometer prior to a dye study.
b. Calibrate all fluorometer at 1 ppb – DWR preference.
c. Calibrate fluorometer prior to taking out in the field, before running samples in the field, and before running samples in the lab

6.1.2. *Sample Collection*

a. Prepare solution standards- Dye standards of known concentrations should be prepared in accordance with the U. S. Geological Survey's dye tracing procedures contained in Turn the fluorometer on and allow it to stabilize for at least 10 minutes.
b. Use a distilled water blank to zero the instrument.
c. Rinse the cuvette with water from the sample bottle before running that sample. Wipe off moisture from the outside of the cuvette.
d. Run samples.
e. Record measurements on the field sheet.
f. Keep samples for future analysis, especially if peak concentration is questionable.

VIII. FLOW MEASUREMENT

1. INTRODUCTION

Stream-flow or discharge is defined as the volume rate of flow of the water including any sediment or other solids that may be mixed with it (Buchanan and Somers 1968). Stream-flow is usually expressed in cubic feet per second (cfs) and discharge flow in million gallons per day (MGD).

Several methods of determining flow are used by DWR. Most consist of wading into the stream with a top-setting flow rod and a vertical axis type flow meter shown as a propeller in Figure 18.

Other methods of determining flows (usually small, low-velocity flows) are:

- Volumetric method
- V-notched weir method
- Estimating flow mathematically method

The USGS maintains many gauging stations across the state and their stream-flow information is available in hardcopy and on-line. Discharge measurements using current meters are based on the equation:

Q=AV, where Q=Discharge, A=Area, V=Velocity

It is as important to get good depth readings as it is to get good velocity readings.

How to Calculate Flow

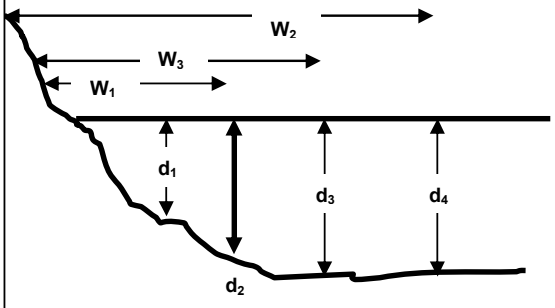
Calculating discharge from each of the width intervals:

$q_2 = v_2 d_2 (w_3 - w_1)/2$

where:
- q_2 = *discharge at width interval 2 (cfs)*
- v_2 = *velocity measure at width interval 2 (ft/sec)*
- d_2 = *depth at interval 2 (ft)*
- w_3 = *distance from the bank or initial measuring point to the point following interval 2 (ft)*
- w_1 = *distance from the bank or initial measuring point to the point preceding interval 2 (ft)*

Calculate the total discharge (flow) as the sum of each of the partial discharges:

$Q = q_1 + q_2 + q_3 + q_4 \ldots q_i$



DWR uses several different current meters and example is shown on Figure 18. The Price meter and the pygmy meter are vertical axis type meters, which use the number of revolutions over a period of time to calculate the water velocity. The Marsh McBirney meter works on the electromagnetics of the water passing by the meter.

Depth-measuring devices are used by DWR include two types of wading rods and a cable-winch bridge board. The top-setting wading rod easily sets the current meter at the proper height. With the other type of wading rod, the depth of the current meter must be calculated and set. The bridge board is used from a bridge handrail or the gunwale of a boat in streams and rivers where the water is too deep or the current is so strong that wading is dangerous or impossible. The winch has a depth-indicating gage.

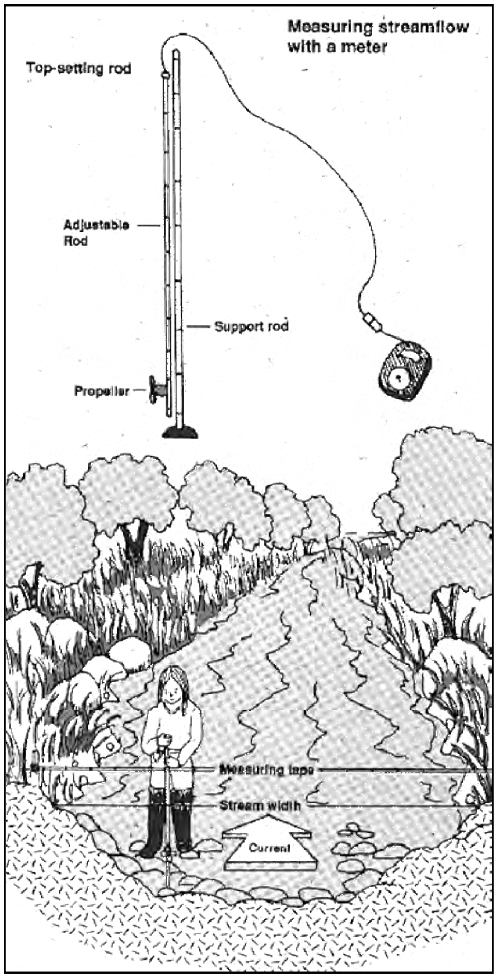


Figure 18. Instream Flow Measurement

2. ESTABLISHING AND USING A REFERENCE POINT

Before measuring any flow a stage reference point (RP) should be found or established. This point can be located on any stationary object over the water surface. Measure the distance from that point to the water surface. It is important to measure this distance before and after doing the flow measurement, as this will indicate any changes in the water level that occurred during the flow measurement.

Many bridges already have an established RP located somewhere on the bridge. These RPs have been established by the USGS and should be used if they can be located. If the RP on the bridge is not located, establish one. Make a mark on a structure over a deep pool near where the flow measurement is made. Clearly identify the mark so that others may use it also.

If many flows are to be done at a station, then a good reference point needs to be used. Each time a flow measurement is performed, record the tape down elevation. As multiple flows are compiled, a relationship between stage and flow can be graphed; eventually allowing flow estimates to be made by measuring the reference point. Occasional flows still need to be performed to make sure the tape down/flow relationship remains constant.

Use a metal tape and dimwap (weight) when measuring the tape down. Stand at the reference point. Let the tape feed out until it barely skims the water surface. Put the tape to the reference point and record the measurement. Be sure to add the length of the dimwap in the measurement.

The reference elevation should be measured to the top of the bolt, the top of the nail head, or to the top of the bridge rail (even if it is beveled). It is important to make your measurements from the exact same point each time.

3. FLOW EQUIPMENT

Price AA current meter
Price pygmy meter
Top-setting wading rod
Headset or beeper box
Stopwatch
100 foot tape measure (in 1/10 ft)
Chaining pins
Stage tape measure with dingwap
Clipboard
Flow sheets
Pencil
Cleaning cloth
Oil
Flagging
Small flathead screwdriver
Hammer and nail
Spray paint (international orange)
Torpedo weights (15 lb., 30 lb.)
Bridge board
Hand calculator

4. FLOW MEASUREMENT PROCEDURE

4.1. Flow Measurement Method

4.1.1. *Pre-Sampling:*

a. Maintain all flow equipment in good working order. Refer to USGS publication, Discharge Measurements at Gauging Stations (Buchanan and Somers 1969).

Note: The spin test is a good indicator of flow equipment readiness.

a. Check condition of flow equipment before leaving the office. An equipment checklist is helpful.

b. Gather all equipment necessary to do the flow, see list in section 3 of this chapter.

c. Select a reach of stream containing the following characteristics:

- A straight reach with the threads of velocity parallel to each other
- A stable stream bed free of large rocks, weeds, and protruding obstructions such as piers, which would create turbulence
- A flat stream bed profile to eliminate vertical components of velocity.
- Wait 15 minutes after moving rocks and vegetation prior to beginning flow measurements to allow stabilization of the stream flow.

d. Establish a stage reference point (RP) (procedure described in following pages).

e. Measure and record the starting stage.

f. Install the current meter on the wading rod, attach the headphones - try a spin test (USGS publication, Smoot & Novak, 1968). Do the headphones click once for every revolution of the current meter? Make adjustments as necessary.

g. Record pertinent information on the flow sheet (See Appendix 7). Include: stream name, date, time start, stage start, location of RP, person doing flow, person recording information, stream conditions.

h. Determine the width of the stream. String a measuring tape across the stream perpendicular to the direction of the flow. Secure the tape on each bank with the chaining pins.

i. Determine how many measurements are necessary to give an accurate total discharge. Measuring velocity at 20-30 equidistant points across the width of the stream is recommended. More measurement points should be chosen

in areas of significant depth or velocity change. Example: More measurements should be made in the area where the flow hugs one stream bank. A rule of thumb is that no area (point) being measured should contain more than 5% of the total flow of the stream.

j. Looking upstream, record from which bank (right or left) the measurements are starting. Record the location on the tape of the starting bank. Example: The left bank starts at 1.5 feet on the tape.

4.1.2. Sampling Techniques

a. Stand downstream and to the side so as not to obstruct the flow of the water to meter.

b. Record the tape measure reading of the point.

c. Measure the depth by placing the wading rod in the stream so that the base plate rests on the streambed. The depth is read from the graduated main rod and is estimated to the hundredth of a foot. Record depth readings on the flow sheet.

d. Use the upper scale of the top setting rod to set the depth of the current meter. At depths of 2.5 feet and less, the average velocity is best measured at a point 0.6 of the depth from the water surface. Using the scale at the top of the wading rod automatically sets the current meter at the desired depth. To set the depth, press the rubber button on the flow rod. This releases the smaller rod. Move the smaller rod until the foot mark on it matches the appropriate tenth marker on the zero to ten scale at the top of the larger rod.

e. At depths greater than 2.5 feet measure the velocity at 0.2 and 0.8 of the water depth (the average of these two velocities will later be recorded as a single value). The top-setting flow rod makes setting these two depths easy. Adjust the top scale readings to one half of the actual depth (this is the 0.8 reading) and to double the actual depth for the 0.2 reading.

f. Start the stopwatch and count the number of revolutions (clicks on the headphones) for at least 40 seconds. Start the stopwatch on count number 0 and stop the watch exactly on a count, not a certain number of seconds.

g. The pygmy meter is rated so that one revolution per second equals to one fps velocity. The Price meter rating is found in the top of the meter box. To use the Price meter table - count a certain number of revolutions: 1, 3, 5, 7, 10, 15, 20, 25, 30, 40 & 50. Compare to the time interval and read the velocity from the rating table. The Price meter also has a connection for measuring very high velocities where a signal is emitted from the meter for every 5 rotations instead of every single rotation.
h. Record the number of revolutions and the time (to the nearest second) on the flow sheet.
i. Move to the next point and repeat steps “a”-“f “until velocities in at least 20 cross sections have been measured.
j. After the final measurement has been made, record the tape reading of the finishing bank.
k. Measure and record the ending stage.
l. Record the finishing clock time.
m. Replace the current meter pivot with the traveling pin and return meter to box to prevent damage while traveling.

5. BRIDGE BOARD METHOD

5.1. Bridge Board Sampling Techniques and Supplies

5.1.1. *Equipment Needs*

- Clipboard with flow sheet and pencil
- Measuring tapes
- Duct tape
- Stage tape and dimwap
- Traffic safety cones and vests
- Bridge board assembly
- Price AA current meter (with tailpiece)
- Torpedo sounding weights (15 lb., 30 lb.)
- Headphones
- Stopwatch

5.1.2. *Bridge Pre-Sampling Setup*

(Refer to Buchanan & Somers, 1969, USGS publication)

a. Assemble bridge board equipment. This involves attaching the assembled Price AA current meter and the appropriate torpedo sounding weight to the hanger end of the winch cable. The current meter's position on the hanger is dependent upon which torpedo weight is used.
b. Attach the headphone jacks to the output terminals of the winch.

c. Do a spin test to ensure that current meter is working properly.
d. Determine the width of the stream and secure the measuring tape to the upstream handrail of the bridge with duct tape. More than one 100-foot tape may be necessary.
e. Determine the distance interval of the 20 - 30 points necessary to make an accurate measurement. Example: Measure velocity every 2 feet on a 50-foot wide stream. Be ready to change the interval if velocity or depth changes significantly. Remember, no more than 5% of the flow in any one interval.
f. Fill out flow sheet information (refer to step in section 4.1.1- "h") of the current meter procedure).

5.1.3 *Bridge Sampling Techniques*

a. Measure the tape down from the reference point.
b. Record the tape reading from the starting stream bank.
c. Move to the first point to measure velocity. The bridge board rests on the handrail (guardrail) of the bridge.
d. Zero the winch depth indicator by lowering the current meter until the cups of the meter are half in the water. Pull the zeroing armature out and rotate until the depth indicator reads zero. Because most bridge handrails are not level, make sure to zero the winch depth indicator at each point that a velocity measurement is made.
e. Measure the depth of the water. To do this, lower the current meter until the cable goes slack. This indicates that the torpedo weight has hit something. Raise and lower the meter a couple of times to get a consistent depth reading for the bottom.
f. Add 0.5 foot to the reading to get the actual depth of the water. This accounts for the torpedo weight that hangs 0.5 foot below the current meter (which was zeroed at the cups). Record the actual depth.
g. At depths less than 2.5 feet, measure the velocity at 0.6 of the water depth (measured from the surface).
h. At depths greater than 2.5 feet, measure the velocities at 0.2 and 0.8 of the water depth.
i. Lower the current meter to the calculated depth.
j. Measure the velocity by counting clicks (revolutions) for at least 40 seconds. Refer to velocity measurements using the Price AA current meter.
k. Move to the next point and repeat steps "d"-"k".
l. After the last velocity is measured, record the measurement of the finishing stream bank.

m. Record the finish time.
n. Measure and record the ending stage.
o. Store all flow equipment properly.
p. Compute the total discharge.

6. BOAT FLOW MEASUREMENT METHOD

Due to the danger because of boat traffic, extreme care should be taken when setting up for boat measurements. Locations where boat traffic is minimal should be chosen and any boats in the area should be warned off.

6.1. Boat Flow Sampling Techniques and Supplies

6.1.1. *Equipment Needs*

- Boat
- Rope (> width of stream)
- Bridge board assembly
- Headphones
- Stopwatch
- Clipboard with flow sheet and pencil
- Hand calculator
- Measuring tape - 100 foot
- Duct tape
- Stage tape and dingwap
- Cross piece assembly

6.1.2 *Boat Flow Pre-Sampling Setup*

(Refer to Buchanan & Somers, 1969, USGS publication Stations for more detailed instructions)

a. Assemble bridge board equipment.
b. Make a spin test.
c. Prepare the boat for work. It takes a minimum of two people in the boat, one to operate the bridge board and one to calculate the meter depths and record the flow information. The cross piece attaches to the bow and holds the boat in position on the rope.
d. Stretch and secure the rope across the stream channel, just over the water surface and perpendicular to the flow direction. Use duct tape to attach the measuring tape to the rope (an alternative is to use a rope marked at regular intervals).
e. Fill out flow sheet information.
f. Determine the interval of sampling points.

6.1.3 *Boat Flow Sampling Techniques*

a. Record the tape measure reading at the starting stream bank.
b. Measure the velocity at first point using the following steps. The bridge board rests on the gunwale of the boat.
   - Zero the winch depth indicator.
   - Lower the current meter until slack in the cable indicates the bottom.
   - Add 0.5 foot to the reading (to correct for the weight that hangs 0.5 foot below the meter).
   - Calculate the depths to set the current meter at 0.2, 0.8 (see step section in 4.1.1- "h") of current meter procedure).
   - Set the depth indicator at the proper depth.
   - Record the number of revolutions and the time interval at each depth.
   - Move boat to next point.
   - Repeat the steps under 6.9 until the entire stream has been measured.
c. Record the tape measure reading of the finishing stream bank.
d. Record the finish time.
e. Compute the total discharge.

7. V-NOTCH WEIR METHOD

7.1. V-Notch Sampling Techniques and Supplies

7.1.1. *Equipment Needs*

- V-notch weir (> stream channel width)
- Vertical staff gage
- Carpenter's level
- Hammers (3 lb., 8 lb. sledge)
- Straight edge
- Graduated container
- Stopwatch

7.1.2. V-Notch Flow Pre-Sampling Setup

a. Determine a good location for the weir plate. Avoid hard rock or loose sandy stream bottoms. Also avoid riffle areas where faster velocities erode the weir plate.
b. Set up the vertical staff gage. The gage should be located in the upstream pool formed behind the weir. Use the carpenter's level to make sure that all faces of the gage are level. Because of the effect of drawdown, the gage should not be located too close to the weir plate.

c. Use the sledge hammer to pound the weir plate into both banks so that the plate dams up all flow in the channel. Use the carpenter's level on all faces of the plate, it must be level. Make sure also that there is no water flowing around or under the weir plate.

7.1.3. V-Notch Flow Sampling Procedures

a. Determine the zero point of the weir (very important reading):

- Use the straight edge and level to measure a level line from the base of the angle on the weir plate back to the staff gage. Or if the distance from the top of the weir plate to the base of the angle is predetermined; then a level line is measured from the top of the plate to the gage and the distance subtracted.
- Read the water level on the staff gage just at the point where the water starts to flow through the notch in the plate.
- Let the water flowing through the V-notch stabilize.

b. Read the staff gage.

c. Determine the difference between the zero point on the staff gage and the water level flowing through the weir plate (read as the water level on the staff gage). This difference is known as head.

d. Look at the flow table for the V-notch weir. Look up the corresponding flow for the particular head height. An alternative to using the flow table is the volumetric method (procedure described in following pages).

e. Periodically clean the weir to prevent the buildup of sediments or solids around the notch. This buildup will affect the accuracy of the weir. Leaves are a problem to a V-notch weir. A leaf stuck at the base of the weir angle can cause a significant rise in water level.

8. VOLUMETRIC METHOD

8.1. Volumetric Sampling Techniques and Supplies

8.1.1. *Equipment Needs*

- Graduated container
- Stopwatch

8.1.2. *Volumetric Flow Procedure.*

a. Mark the container to a known volume (examples: 1 gallon, 1 liter).
b. Place the container under the discharge, collecting all flow.
c. Time the interval needed to fill container to the volume mark.
d. Empty the container.
e. Repeat steps “b”-“d” several times.
f. Average timed results.
g. Calculate the flow rate as flow volume/time. Example: 1 gallon in 15 seconds.
h. Convert flow to cfs or MGD.

9. MARSH MCBIRNEY MODEL 201 CURRENT METER

The principles of using the Marsh McBirney current meter are the same as using other current meters. The meter employs the velocity/area method of flow measurement. The sensor probe detects water velocity. The panel meter reads velocity in feet per second. The procedure for using the Marsh McBirney meter is the same as that described in Section 4 (Flow Measurement Procedure) but no calculations are needed as the flow is directly read on the instrument’s screen.

This meter is used to measure small flows/low velocities. Because the probe has no moving parts, debris in the water has little effect on the reading. Another advantage is that the sensor probe attaches to the top-setting flow rod.

10. FLOW SHEET CALCULATIONS

10.1 Data Form

10.1.1. *Data to be Recorded on Data Sheet*

- Distance from the initial point
- Depth
- Time (in seconds)
- Revolution

10.1.2. *Calculations*

a. Columns titled, velocity (mean in vertical), area, width, and discharge are calculated values.
b. Calculate the width of each cross section. The width of the section is the sum of one-half the distance from the point of measurement to each adjacent point. Example: In the first

section the width is one-half the distance to the adjacent point plus one half the distance to the stream bank.

c. Calculate the velocity in each cross section. In depths of greater than 2.5 feet, two velocity measurements are taken in each cross section (0.2, 0.8). Average the two readings and record in column. This depends on the current meter in use:
   - The Price pygmy meter - the number of revolutions divided by the seconds.
   - The Price AA meter - The velocity is taken directly from the meter rating table. Not all Price AA meters use the same rating table-be sure that you have the correct table for the meter you are using.
   - The Marsh McBirney meter - The velocity is read from the panel as feet per second.

d. Calculate the cross-sectional area. Multiply the width times the depth.

e. Calculate the discharge of each cross section. Multiply the cross-sectional area by its velocity.

f. Calculate the total discharge of the stream. Add all the cross-sectional discharges together.

g. Record the average velocity of the stream. Divide the total discharge by the total area.

11. OPEN CHANNEL FLOW MEASUREMNT METHOD

11.1 Introduction

The following section provides a brief overview of methods for determining flow in an open channel. For more detailed information regarding open channel flow measurements, refer to the references section.

Open channel flow can be defined as flow in any channel in which liquid flows with a free surface. Open channels are generally used in moving fluids at most municipal treatment facilities, industrial waste treatment operations and in most irrigation applications. An open channel can also be a stream or a ditch. Open channel flow is typically measured by the use of a calibrated restriction device placed in the channel that affects the surface level of the liquid as it moves past the restriction. This type of open channel measuring device is referred to as a "primary" device. The known dimensions and physical characteristics of the restriction device are used to correlate a relationship between water surface level and flow. After the water level/flow relationship has been established, the flow in the open channel can be easily measured by manually sighting the height of the liquid's surface level against a calibrated scale (staff) and then referring to the appropriate rating curve or table.

The following are the most commonly used types of "primary" open channel flow measuring devices, (restriction devices):

11.1.1 Weir: a dam constructed across an open channel, over which liquid flows through an opening or notch. The most commonly used types are rectangular, trapezoidal and triangular.

11.1.2. Flume: a specially shaped open channel, designed to change the channel area or slope, resulting in an increase velocity and surface level of the liquid flowing through it. The most commonly used types are: Parshall and Palmer-Bowlus

11.2 Flow Meter

a. A flow meter is a mechanical device used to measure the liquid level in the channel and convert the level into a corresponding flow rate
b. A stage recorder is a mechanical device used to record the surface level of the liquid over a period of time

Note: Measuring flow in an open channel by means of a weir or flume is a simple function of surface level and is the most basic and inexpensive method available. However, if continuous stage or flow recording is required, then the use of a stage recorder and/or a flow meter in conjunction with the primary device may be necessary. Some of the more commonly used methods employed by these devices to determine the surface level of a liquid are floats, dipping probes, ultrasonic sensors, and bubblers.

IX. BATHYMETRY

1. PROCEDURES

Recording fathometers are used to provide bathymetric traces of water depths. Since water depths are time dependent (especially in tidal areas) the date and time of all traces should be noted. Operating manuals provide operation and calibration procedures to be followed. In particular, tide and draft adjustments provide calibration in regard to the respective tidal amplitude and sensor probe depth. All traces should be noted with transect description, chart speed, direction of travel, and pertinent reference points and then indexed to a site map. When working in tidal areas, a water stage recorder should be positioned to provide a histogram of water levels to correlate with the bathymetric trace.

During the initial setup of each survey, the fathometer calibration should be checked against a field measurement of water depth made using a graduated sounding line.

2. EQUIPMENT AVAILABLE

The following equipment is available for bathymetric surveys:

- Water level recorder and/or referenced gauging stations(s)
- Depth gauge
- Calibrated sounding line(s)

3. SPECIFIC EQUIPMENT QUALITY CONTROL PROCEDURES

Number all equipment and keep a record of maintenance and calibration procedures. Use the following steps to maintain and calibrate bathymetric measurement equipment:

3.1. Recording fathometers:

3.1.1. Calibrate and maintain according to the manufacturer's instructions before use. The chart speed should be checked against a reliable time source before the instrument is sent to the field.

3.1.2. Check daily in the field against a field measurement of water depth using a calibrated sounding line.

3.1.3. Clean daily after use and before storing.

3.2. Sounding lines are to be calibrated against steel surveyor's chain and shall be accurate to 0.1 foot.

X. WATER QUALITY VESSEL OPERATION

Water quality investigations frequently require DWR personnel to work in locations that are accessible only by boat. This necessitates that field staff be thoroughly trained in the safe operation of those boats and become familiar with the general maintenance and the particular operation of each vessel. This boating SOP provides a general operating guide to ensure that all boating and trailering activities are carried out in a safe manner and that all boats and motors are operated in a manner that reduces the frequency of repair. All field personnel should read and thoroughly understand this SOP prior to operating any DWR boat.

1. BOAT SAFETY

1.1. Supplies Needed On-Board

1. ***Fire Extinguishers*** - before operating boat, familiarize yourself with where the fire extinguisher is located. Check to make sure that it is fully charged.
2. ***Sound Producing Devices*** - boats should be equipped with a can type air horn or a manually operated whistle.
3. ***Paddles or Oars*** - all boats should be equipped with oars or paddles.
4. ***Visual Distress Signals*** - when operating boats in coastal waters, the boat must be equipped with a flare kit. The kit should include hand held flares and a flare gun for aerial type flares.
5. ***PFD's (Personal Floatation Devices)*** - **all DWR employees are required to wear life preservers at all times while on board DWR boats.** Boats will be equipped with a type 1, 2, or 3 PFD of suitable size for each person on board and a throw-able floatation device (throw cushion, flotation ring).
6. ***Lights*** - when operating a boat at night, the boat must display the front green and red navigational light and the rear beacon light. If planning to operate at night, the lights should be checked before leaving the loading area.

1.2 Safety Check

1. ***Weather*** - check weather reports before leaving shore and remain watchful for signs of bad weather. Tune into the National Weather Service Report, on a Marine radio, periodically to check weather conditions, small craft advisories, gale warnings, etc. Do not go out on the water during lightning storms.
2. ***Care and Maintenance*** - all equipment and supplies should be properly secured. Keep decks and other spaces clean, free of clutter and trash. The vessel should be free of fire hazards with clean bilges and in good condition. Inspection and required maintenance on a regular schedule will ensure the hull and superstructure remain sound.

Ensure all repairs are made properly and with marine rated parts. Always carry a toolbox and know how to make minor repairs.

3. ***Communications*** - when operating in remote areas it is always a good idea to bring along a cellular phone for cases in which assistance may be needed. Two-way radios should be used when operating with two or more boats. When operating in coastal waters always bring along either a hand-held portable marine radio or a fixed mounted marine radio.

2. FIXED MOUNT/CONSOLE TYPE BOATS

2.1. Trailering

2.1.1. *Pre-Trip Check and Preparation*

a. Install 1 ⅞ or 2" trailer ball to trailer hitch depending on the trailer.
b. Unscrew clamping mechanism on boat trailer tongue.
c. Back vehicle up to boat trailer, with trailer tongue directly over the center of the trailer ball.
d. Lower trailer jack so that the trailer tongue fits over the trailer ball.
e. Screw down, or tighten, the clamping mechanism (all the way) onto the trailer ball. Lock with a 2640 Master Lock.
f. Hook up both safety chains by crossing the chains and hooking to holes on the trailer hitch. Do not tow boat without safety chains.
h. Hook up brake line cable to eye bolt attached to the vehicle.
i. Plug in trailer lights and check the lights for proper operation.
j. Secure gunwhale boat strap.
k. Check the bow eye to make sure safety chain is hooked up and winch is locked down securely.
l. Periodically check the clamping mechanism on the trailer tongue to assure that it is screwed down all the way.
m. Conduct an inspection walk around the boat and trailer:
    1) Test to see if the boat motor starts before traveling.
    2) Check level of the engine oil on 4-cycle boat motors.
    3) Check the trailer tire pressure and adjust if necessary.
    4) Check the condition of the axel grease. Add grease as needed.
n. When traveling, stop and check the trailer and boat; retighten boat straps as needed. Feel the trailer bearings to see if they are hot. If hot, they probably need to be greased or replaced.
o. Trailer slowly over speed bumps and holes.

p. When backing into parking areas, do not let back of trailer come in contact with curb to avoid damaging license plate bracket or trailer lights.

2.2. Boat Launching

2.2.1. *Unloading*

a. Upon arrival at the boat ramp check the ramp to make sure it is suitable for launching including checking that the water level is high enough for proper launching.
b. **Install all the boat plugs**; check inside the bilge to make sure that the plug is installed.
c. Remove the boat strap.
d. Load the boat with equipment.
e. Unplug trailer lights
f. Make sure the motor is in the "up" position before launching the boat.
g. Keep winch "locked" until boat is in the water.
h. When the boat is in the water lower the motor and then start the motor (see motor operating instructions).
i. While one person is operating the boat another person should be manning the trailer winch.
j. Unhook winch cable from bow eye, but do not remove safety chain until the boat is running and idling.
k. If needed, back the vehicle up slightly and press the brake to bump the boat off the trailer.
l. When boat is clear from the trailer, pull the vehicle out of the ramp **slowly** and park it.

2.2.2. *Loading*

a. Slowly back the trailer into the water so that the center "guide roller" is visible above water.
b. Line up the boat with the trailer and **very slowly** ease the bow of the boat onto the center roller. If boat is off center of the trailer, back up and try again.
c. **Do not** approach trailer at a speed that will damage the boat hull or trailer if the center roller is missed!
d. The person manning the trailer winch should signal the boat operator to go left or right, or to tell the boat driver to back off if they are going to miss the center roller.
e. Once the bow is on the center roller, slowly advance the boat up onto the trailer as far as it will go. If it does not reach the stanchion then hold the boat in position until the person manning the winch can get out enough cable to hook to the bow eye.

f. Once the cable is hooked and tension is maintained then power down the motor and cut it off.
g. Winch the boat onto the trailer until the bow is snug against the stanchion.
h. Lock down the winch gear.
i. Raise the motor to the "up" position and flip down the tilt lock bar, then lower the motor until it presses against the tilt lock bar.
j. **Slowly** drive out of the boat ramp to the parking lot.
k. Remove the boat plugs.
l. Unload the boat.
m. Hook up boat strap.
n. Plug in trailer lights.
o. Make sure that all aerials and/or bimini tops are down.
p. Walk around trailer and **double check everything!**

2.3. Boat Operation

2.3.1. *Fueling*

a. Fill oil reservoir to required fill level with appropriate motor oil.
b. When fueling boats with 2 cycle outboard motors without an oil reservoir add one pint of 2 cycle outboard motor oil to the gas tank for every six gallons of gasoline. Use marine fuel stabilizer in all fuel tanks.
c. Fill tanks to their maximum fill level.

2.3.2. *Motor Operation*

a. Switch the battery "PERKO" switch to the "ALL" position.
b. Pump the gas primer ball until it is tight.
c. Lower motor into the water using hydraulic trim switch on the throttle lever.
d. When starting "cold" the choke must be engaged. To engage choke, push the ignition key in as far as it will go, then turn the key clockwise until the motor starts. If motor does not start within five seconds **do not** continue to engage the starter. Re-pump the primer ball and try again.
e. Once the motor starts disengage the choke and let the motor idle.
f. Once the motor has been given ample time to warm up, back the boat off the trailer.
g. Let motor idle down before changing from reverse to forward. Between forward and reverse, make a brief stop in neutral.
h. If working in open water with ample depth for boat running, advance the throttle to plane out the boat, adjusting the trim if necessary.

i. Once proper plane is achieved, throttle the boat back to 3/4 (approximately 4200 rpm) throttle. **Do not run the boat at full throttle.**

3. SMALL BOATS WITH PORTABLE MOTORS

3.1. Trailering

For the most part the same rules apply that were covered in the previous section with a few exceptions:

a. Install appropriate sized trailer ball to trailer hitch.
b. Flip down locking switch on trailer tongue and lock with a 2640 Master padlock.

3.2. Boat Operation

3.2.1. *Fueling*

a. Obtain gas tank from storage cabinet.
b. Make sure the tank selected is equipped with the proper fuel line connections for the motor you will be using.
c. Most of the fuel tanks have a capacity of 6.6 gallons. Leave some head space in the fuel tanks - **do not overfill**.
d. Add one pint of 2 cycle outboard motor oil for every six gallons of gasoline unless motor requires different oil and ratio.

3.2.2. *Motor Operation*

a. Select the proper motor for the boat that is to be used.
   - 5 hp for Jon boat and 12' Alumacraft,
   - 15 or 25 hp for 14' Alumacrafts.
b. Place outboard motor in the **center of the transom** and completely tighten the clamping screws on the outboard motor.
c. Place tank in boat and connect to motor to assure proper fitting.
d. Run a chain through the gas tank handle, then through the handle on the outboard motor, and then through the hole in the boat and lock with a pad lock.
e. Secure the motor to one side with a bungee cord to keep motor from swaying back and forth while going down the road.
f. To run: connect fuel line to motor, and pump primer ball.
g. Pull choke knob if motor is "cold".
h. Turn tiller throttle lever to "start" position.
i. Pull starter cord. If motor does not start after one or two pulls then pump the primer ball and try again.
j. Once motor starts push choke lever in and let run for about a minute then idle down with throttle lever.

k. To put motor in gear, make sure motor is idling low and pull the gear lever forward to go in a forward direction. To go in reverse, push gear lever backward to reverse position with a brief stop in neutral.

l. Once motor is in gear then throttle up the motor, once the boat is planned out back off of the throttle about 1/4 turn.

m. **Do not run the motor at full throttle, run at 3/4 throttle.**

n. To turn the motor off, press the red kill button located next to the choke lever. On some motors the kill button is located on the end of the tiller.

4. TROUBLESHOOTING: FOR ALL BOATS

4.1. Problem - **No power to starter**

a. Check to see if "PERKO" switch is on the "ALL" position.

b. Check to see if throttle lever is in neutral.

c. Check battery terminal connections.

d. Check main fuse in outboard motor.

e. Check fuses inside console.

4.2. Problem - **Motor is Turning Over But Will Not "Fire" or Start**

a. Check to see if gas line is connected to motor.

b. Check to see that primer ball has been pumped until tight.

c. Check to make sure "deadman's" or kill button is clipped.

d. Make sure air vent screw is open on gas can.

e. Check spark plug wires, replace spark plugs (they may be fouled)

4.3. Problem - **No Water is Coming Out of Flow Hole**

a. **Do not** continue running motor. Shut down and attempt to unclog flow hole with a coat hanger or similar object.

b. If problem persists, do not use boat. If out on the water when this occurs, get towed back to boat ramp.

4.4. Problem - **Extreme Cavitations or "Porpoising"**

a. Adjust trim with up and down button on throttle lever.

b. Make sure there is not an excessive amount of water in bilge.

c. Adjust the weight distribution of equipment and personnel in the boat (trim the boat up and shift weight).

XI. LAKES SAMPLING

Field data collection procedures for reservoirs and lakes differ from that of streams and rivers due to the differences in water depth and hydrology. This section focuses on procedures specific to physical and chemical water quality sampling of lakes.

1. FIELD PREPARATION

1.1. Pre-Sample Preparation

a. Preparation of the lake sampling packet.
   1. Sample tags and lab sheets must be legibly hand written with permanent black ink. Adhesive labels for the sample tags may be prepared on a laser printer.
   2. Include maps showing the locations of the sampling stations. Electronic copies of lake maps are on the ISB shared drive (Lake Maps folder).
   3. Include a copy of the Field Observation form (Figure 19).
   4. Include special instructions and point-of-contact information as needed.

b. Contact responsible parties at all publicly owned lakes several days in advance of sampling. Contact names are in the particular lakes file or in the Lakes Database. Changes in contact information will be noted and provided to the Lakes Database Administrator so that the database can be updated.

c. Confirm availability and working condition of boats, motors, vehicles, and Hydrolab/YSI.

d. Verify the lake stations on the map with the station numbers on the lab sheets and tags.

e. Always include extra bottles in case of accidents, defective bottles, and/or discovery of algal blooms or other environmental conditions that justify additional samples.

1.2. Field Equipment Needed

Aquatic Plant & Algal Bloom Report Forms	Cooler(s) with ice
Field Observation & Stratified Data Forms	Lab Sheets and Tags in sealed bag
Preservatives- Lugols solution, H_2SO_4, HNO_3	Hydrolab/YSI Meters
Labline with Rope	Camera
Sample Bottles	Calibrated backup meters
Pens and Pencils	Maps
Life Jackets	Boat Oars
Gas Tank for boat	Boat Plug & Anchor
Winter- cold weather suit (as needed)	First aid/safety box

Electric motor & 2 fully charged batteries (if needed)
Secchi Disc with line marked in 1 centimeter increments

Calibration Materials-(*e.g. Calibration and D.O. sheets, pH and conductivity standards, meter manuals).*

1.3. Field Sheets

a. *Stratified Field Sheets*: Make sure that stratified field sheets (Figure 5, page 25) are carried to the lake stations along with pens or any non-erasable ink for writing and a clipboard. Clearly write the station number, date, time, depth, dissolved oxygen, temperature, pH, conductivity, and secchi are recorded on the field sheet. At the top of the field sheet record, the name of the water body, which meter is used, and the names of the field samplers is also recorded.

b. *Field Observation* Form: In addition, a separate form is to be filled out for all of the ambient lakes (Figure 19). This form requests information about the use support status, restoration activities, weather conditions, the watershed, and lake water quality.

c. After sampling, both of these forms are filed in the current lake files in the Intensive Survey Branch. Data are entered into the lakes database within 72 hours of the lake trip.

FIELD OBSERVATION FORM Lake Name _____
Page 1 of 2 Samplers' Name: _____Date: _____

WEATHER CONDITIONS

Air Temperature	% Cloud Cover	Wind Direction (from)	Wind Velocity	Rainfall (last 48 hrs)
__ <60º	__ 0-25%	_____	__ <10 mph	__ None
__ 60-70º	__ 25-50%		__ 10-20 mph	__ < ¼ inch
__ 75-90º	__ 50-75%		__ >20 mph	__ ¼ - 1 inch
__ 90º	__ 75-100%			__ >1 inch

SHORELINE AND WATERSHED OBSERVATIONS
Please describe *development* around the lake shore:

Type of Development	Density/Intensity	% of Shoreline Developed
__ Residential/Urban	__ Slight	__ 0-25%
__ Commercial/Industrial	__ Moderate	__ 25-50%
	__ heavy	__ 50-75%
		__ 75-100%

Please check *land uses* observed in the watershed:
- __ Agriculture (specify if possible)
  - __ Crop production
  - __ Pasture land
  - __ Feedlots/Animal production
- __ Forest
- __ Wetlands
- __ Urban/Residential
- __ Commercial/Industrial

LAKE QUALITY
Please check the one statement that best describes the *physical condition* of the lake water today:
- __ Crystal clear water.
- __ Not quite crystal clear, a little algae/suspended sediment visible.
- __ Definite algal greenness, yellowness, or brownness apparent.
- __ High algal/sediment levels with one or more of the following: floating scums on lake or washed up on shore; strong foul odor; or fish kill.

Please check the one statement that best describes the *aquatic macrophyte* community:
- __ None observed
- __ Small amount of vegetation evident along shoreline and/or headwaters of the lake; <25% of the lake's total surface area covered.
- __ Macrophytes extend out from shoreline well into the lake; 25-50% of the surface area covered.
- __ Dense growths of several species cover more than 50% of the surface area.
- __ Nuisance levels of a singe species cover more than 50% of the surface area.

Please check the one statement that best describes your *opinion* of how suitable the lake water is for recreation and aesthetic enjoyment today:
- __ Beautiful, could not be nicer.
- __ Very minor aesthetic problems; excellent for swimming, boating, enjoyment.
- __ Swimming and aesthetic enjoyment slightly impaired because of levels of algae/sediment/or weeds (please indicate which).
- __ Desire to swim and level of enjoyment of the lake substantially reduced because of algae/sediment/or weeds (please indicate which).
- __ Swimming and aesthetic enjoyment of the lake nearly impossible because of algae/sediment/or weeds (please indicate which).

Figure 19. Field Observations Form

LAKE NAME: _____
Page 2 of 2

Designated Use Classification: _____

_____

Supplemental Classification: _____

USE SUPPORT STATUS
Designated uses appear to be:

__ Fully supported.
__ Fully supported, but threatened (impairment could result if pollution controls are not implemented).
__ Partially supported
__ Not supported

If uses are not fully supported, what pollutants or conditions are *causing* impairment (check all that apply):

__ Nutrients
__ Situation
__ Flow alteration
__ Suspended solids
__ Noxious aquatic plants
__ Organic enrichment/low DO
__ Thermal modification
__ Filling and draining
__ Other (please specify)

If uses are not fully supported, what *sources* of pollutants contribute to use impairment:

POINT SOURCES
__ Industrial
__ Municipal
__ Municipal pretreatment
__ Other point sources (specify)

NONPOINT SOURCES
__ Agriculture (specify if possible)
  __ Crop production
  __ Pasture land
  __ Feedlots
  __ Aquaculture
  __ Other (specify)
__ Silviculture
__ Construction/Land development
__ Urban runoff
__ Mining/resource extraction
__ Land disposal of waste (e.g. landfills, wastewater and sludge application, on-site septic tanks, etc.)
__ Hydrologic/habitat modification (e.g. canalization, dredging, flow regulation, etc.)
__ In-place contaminants
__ Recreational activities (e.g. motor boating)
__ Other nonpoint sources (please specify):

__ Source of impairment unknown

RESTORATION ACTIVITIES
Please describe any lake restoration or water quality management activities that have taken place:
_____
_____
_____
_____

Figure 19. Field Observations Form (continued)

XI. LAKES SAMPLING

2. LAKE DATA COLLECTION

2.1 Lake Physical Data Collection Methods

a. Secchi depth measurement is taken as described in Chapter III, Section 6.

b. Dissolved oxygen, water temperature, conductivity and pH are measured with a multiprobe (Hydrolab) meter beginning at the surface of the lake (0.15 meters from the surface).

c. From the surface to either the bottom of the lake or to a depth of 10 meters, physical measurements are recorded at 1- meter increments

d. Below ten meters, physical measurements are recorded at 5-meter increments until the bottom of the lake is reached

2.2. Lake Water Sample Collection

2.2.1 *Description*

a. Samples will be collected at the surface, photic zone, or at the bottom, which are described below and in detail in Chapter I.

b. If "SUR" is part of the station number, the sample is to be collected at the surface. If 'BOT" is part of the station number, the sample is collected one foot above the bottom. If "SUR" or "BOT" doesn't accompany the station number, the sample is collected in the photic zone.

c. As with all samples for laboratory analysis, a lab sheet must be completed as described in Chapter II,Section 1 of this SOP.

d. Detailed definitions of these parameters and methods of collection found in Chapter I, Section 3.

2.2.2. *Types of Typical Lake Samples*

a. **Surface Grab** samples (chloride, hardness, fecal coliform bacteria, and metals) are collected 0.15 meters below the water's surface and this can be done by hand dipping the bottle. The bottle top and bottle opening should be protected from contamination. Grasp the bottle near the base and plunge it mouth down into the water, avoiding surface scum. Position the bottle away from the hand of the collector, the shore, the side of the sampling platform, or boat.

b. **Photic Zone** – the photic zone is defined as the column of water in the lake from the surface down to a depth equal to twice the secchi depth measurement. Photic zone samples (residue, turbidity, chlorophyll *a*, nutrients, and phytoplankton) are collected by raising and lowering the Labline at a steady speed within the photic zone until it is full. A description of this procedure is given in this SOP in Chapter I, Section 3.2.3.

c. **Bottom sampling** (nutrients) is accomplished by inserting the two plugs in the top of the Labline and lowering it just above the bottom of the lake. This needs to be done gently as not to stir up sediments on the bottom. The plugs can be released by firmly jerking the rope on the Labline. Wait until the Labline if full before bringing it back to the surface. This can be determined by observing air bubbles from the sampler rising to the lake surface, the stopping or feeling the weight of the Labline at the end of the rope.

2.2.3 *Field Records and Information*

a. **Photographs** are to be taken of various locations on each sampled lake to record the shoreline and lake characteristics. In particular, an unusual shoreline/ watershed activity, aquatic plants, algal blooms, or other water quality issues are to be photographed (photo number and brief description and location of where picture was taken) must be made. This information along with the camera, are to be returned to the Lakes Database Administrator upon return to ISB.

b. **Comments and questions** from citizens, lake managers, water treatment plant supervisors, etc. are to be recorded (written) along with contact information and individual's name and title (if any). This information will be submitted to the the Lakes Database Administrator upon return to ISB.

2.3. Typical Lake Sampling Parameters

Below is a list of typical lake water sample types. Descriptions on how samples are preserved and collected are found in Chapter I, section 3, section water samples as well as more detailed descriptions can be found in this SOP in the Sample Collection Section (Chapter IV).

2.3.1. *Physical Parameters include*

Conductivity	Dissolved Oxygen (mg/L)
pH	Temperature (°C)
Secchi Depth	

2.3.2. *Chemical Parameters include*

Nutrients	Residue
Turbidity	Chloride
Magnesium	Calcium
Metals	Chlorophyll *a*

*Additional parameters may be collected based on specific lake conditions and/ or requests

2.3.3. *Biological Parameters*

a. Fecal coliform bacteria: Water samples are collected at the surface of the lake.

b. Phytoplankton: Water samples are generally collected as a photic zone sample. Bloom samples may be collected at the surface of the lake, as needed.

c. Aquatic Plants: Use the Aquatic Plant Report Form supplied by the Ecosystems Branch of the Environmental Sciences Branch and submit it along with a specimen if there appears to be problematic aquatic plants or for identification. Refer to the Aquatic Plant Report Form for collection and preservation of aquatic weeds. Include a map of the location showing where the plant specimen(s) were collected.

d. AGPT (Algal Growth Potential Test): These samples are collected after consultation with EPA since they perform the tests. The bottles (1 liter) are furnished by EPA as are the tags and coolers. The samples are collected in the photic zone and no preservative is used. The samples are shipped back to the EPA Athens, GA laboratory for analysis. The address and telephone number is: Bob Quinn, U.S. EPA, Region IV, Environmental Services Division, Athens, Georgia 30613, (706) 546-2420.

2.3.4 Lab and Field Sheets: All lab and field sheets should be **legibly** filled out with applicable dates, times, depths, etc.

a. The same time is recorded on both field and lab sheets for the same station. A field observation sheet should also be filled out and any other notable features recorded.

b. Any notes of unusual observations of lake water quality or shoreline activities that could impact water quality should also be submitted.

c. Field sheets and filed observations sheets along with camera are to be submitted to the Lakes Database Manager upon return from the field.

3. LAKE DATA MANAGEMENT

3.1 Data specific to the Intensive Survey Branch Lake Monitoring Program are warehoused in the Lakes Database. This database is maintained by the Lake Database Administrator. The responsibility of the Lake Database Administrator includes entry of data, verification data entry accuracy and reporting issues related to the functioning of the database to the ESS IT staff.

a. Physical field data are entered into the ISB's Lakes Database within 24 hours of receipt from the field sampling team.

b. Chemistry results from the DWR laboratory are entered into the Lakes Database within 72 hours of receipt from the laboratory.

c. Lake data which have been entered into the Lakes Database but not checked for input accuracy and/or completeness are designated ‘P’ for ‘Provisional’.

d. Lake data which has been reviewed and verified for input accuracy and completeness are indicated with the designation ‘A’ for ‘Accepted’.

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XII. SEDIMENT OXYGEN DEMAND

1. GENERAL DESCRIPTION OF SOD TEST

Sediment Oxygen Demand (SOD) is one of the more significant variables in water quality modeling evaluations for determining stream assimilative capacity. SOD data are primarily used for waste-load allocation purposes in the evaluation of receiving waters.

The SOD test involves placing an SOD chamber on the bottom sediment, securing it to prevent water infiltration and monitoring oxygen change within the chamber. A dissolved oxygen sensor inside the chamber measures the rate of decrease in oxygen that is used by organic materials in the bottom sediments over a given period of time. A standard SOD test includes seven SOD chambers of which two are water column control (blank) chambers and five are replicate SOD chambers (Figure 20). The blank chambers, used to determine water column respiration rate, have bottom plates that prevent bottom sediment from contacting the water in the chamber. The SOD replicate chambers have open bottoms allowing the internal water to circulate over the bottom sediment. The rate of oxygen change in the replicate SOD chambers minus the water column respiration of the blank chambers equals the SOD rate.

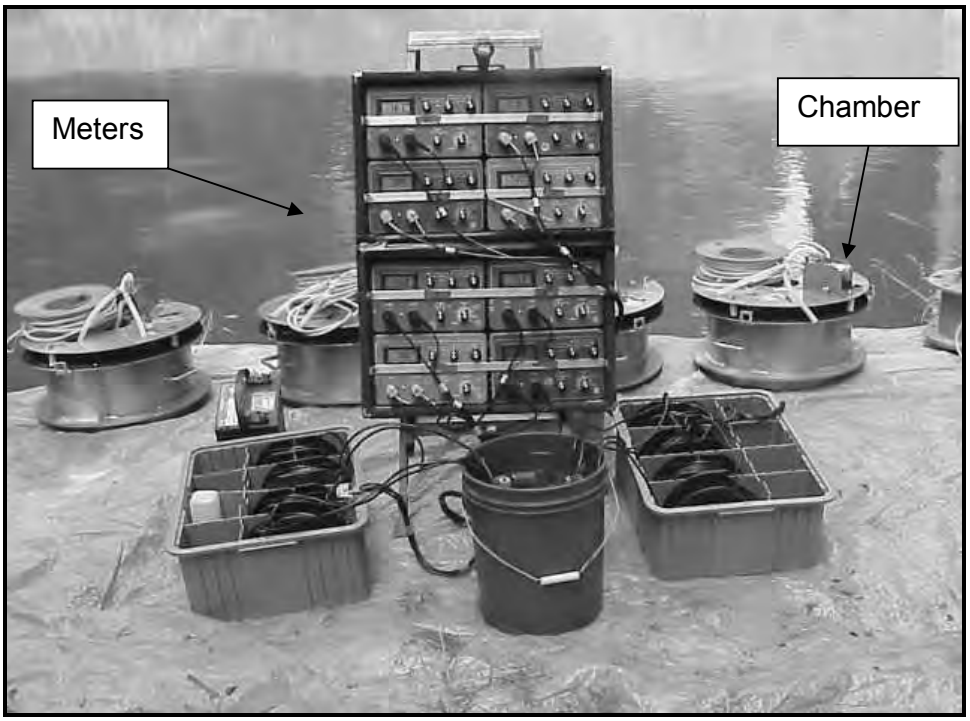


Figure 20. SOD Equipment

1.1. SOD Rate Formula:

The SOD rate for any study location is then calculated by using the SOD rate formula:

$$ß \times (K \times V) \div A = gr\ 0_2/m^2/hr.$$

where: ß = rate of change in D.O. as mg 0_2/L/min.

V = chamber volume in liters

A = chamber area in meters square

K = 0.06 (constant) converts liters to square meters

SOD rates are dependent on benthic metabolic processes, sediment particle size, stream velocity and other factors. SOD rates from 77 in-situ tests performed at locations with various substrate compositions are presented in Sediment Oxygen Demand, Processes, Modeling and Measurement (Murphy and Hicks, 1986, p. 318). An example SOD Excel Worksheet is provided at the end of this section for reference.

1.2. SOD Equipment List – Due to the amount of gear and equipment necessary to successfully complete SOD tests, a checklist is recommended when preparing for testing. See Figure 21.

1.3. Site Evaluation – Each site should be visited and checked out to determine if sediment is suitable in the area under investigation. Figure 22 is the SOD Site Evaluation Form that should be completed for each location.

2. FIELD CALIBRATION DISSOLVED OXYGEN METERS

An initial calibration is performed on the YSI 58 meters prior to the SOD test and a terminal calibration is performed on the meters after the test is completed. All calibration data is recorded on the SOD Calibration Forms (Figure 23). The need for accuracy is paramount for SOD evaluations due to the extremely small increments of change in D.O. measured during the test (+/- 0.01 mg/L). Because of the number of meters being calibrated on site and the extreme accuracy required for SOD testing, initial and terminal calibration procedures in this section vary from other D.O. meter calibration methods in this document. SOD meters are calibrated using the Modified Winkler Azide method as opposed to saturated air calibration methods.

Figure 21. SOD Equipment List:

CHAMBERS:
___ FIVE REP CHAMBERS ALUM
___ TWO BLANK CHAMBERS ALUM
___ ONE CLEAR BLANK CHAMBER
___ TUBES ON CHAMBERS
___ FLOW RESTRICTORS IN TUBES
___ SPACERS ON CHAMBER
___ BATTERY CLIPS ON DC LEADS
___ RUBBER SEALS OK
___ SILICON SEALS OK
___ TEST PUMPS
___ CHAMBER COLLARS
___ 3 BATTERIES MINIMUM (CHARGED)
___ CHAMBER HARNESS AND FLOATS
___ STOPPERS -#1 & #11½

METERS:
___ DO METERS
___ NEW MEMBRANES ON PROBES
___ CONDO METER
___ MEMBRANES & ELECTROLITE KIT
___ 100' CABLES WITH PROBES
___ EXTRA 50' CABLE AND PROBE
___ CALIBRATION & SOD FIELD SHEETS
___ COPPER BATTERY BARS
___ STAND FOR METERS (BOAT OR BANK)
___ "C" CLAMPS (LARGE) - BOAT METER STAND
___ BUNGIES FOR METER STAND
___ BOARD FOR METER STAND MOUNT

WINKLER
___ WINKLER KIT (CHECKED OUT)
___ EXTRA CHEMICALS
___ BURET AND GLASSWARE
___ EXTRA BURET AND GLASSWARE
___ BUCKET FOR CALIBRATION
___ WATER CALIBRATION
____BURET STAND
____BURET WIRE
____STARCH

PERSONAL EQUIPMENT
____RAIN GEAR
____BOOTS
____WATCH
____COOLER AND ICE
____WASH WATER/SOAP
____INSECT REPELLANT
____SUN SCREEN
____HAT
____SUN GLASSES
____FOOD/DRINKS/WATER

MISC. EQUIPMENT
____CAMERA AND ACCESSORIES
____SEDIMENT JARS AND TAGS
____SOD TOOL BOX
____MAPS
____CALCULATOR/PENCILS
____TARPS
____FIRST AID KIT
____MACH, SHOVEL
____CHAIRS, BOX
____ROPES FOR BANK OR BOAT
____CELL PHONE
____COLORED TAPE
____BATTERY TESTER
____"C" CLAMPS (SMALL) FOR REP LIDS
____FIELD LOG FOR SOD TEST
____PLASTIC CRATES

SOD SITE EVALUATION

Site Location - _____
_____

Date: _____ Time: _____

Site Description - _____
_____
_____
_____

Topo Map # _____ % From Right Bank (facing US) _____

Weather - _____
_____

Bank Description - _____
_____

Depth - _____ Velocity (fps) -_____

Sediment Description - _____
_____

Bottom Topography - _____

Water Description (turbid, clear, etc.) _____
_____

Site Schematic:

Figure 22. SOD SITE EVALUATION FORM

All meters are to be air calibrated prior to field operations (and on-site calibration) to assure all meters are functioning properly and stabilized.

The procedures are as follows:

2.1. Calibration Procedures

2.1.1 *INITIAL CALIBRATION Method*

a. Turn off all electronics (cellular phones, depth finders, etc.) prior to reading and calibrating meters.

b. Connect the D.O. probe to the probe receptacle of the YSI 58 meter and screw the retaining ring finger tight.

c. Connect the D.O. stirrer to the stirrer receptacle of the YSI 58 meter and screw the retaining ring finger tight. Check the stirrer battery condition by turning the stirrer switch to its spring-loaded battery check position. The warning LOBAT will indicate when approximately 5 hours of battery life remain.

d. Zero the instrument. Set the function switch to ZERO and adjust the display to read 0.00 with the O_2 ZERO control.

e. Switch to the 0.01 mg/l position and wait at least 60 minutes for the probe to polarize. Allowing additional time to re-polarize the probe is necessary whenever the meter has been turned off or the probe has been disconnected.

f. After the 60 minute wait, turn the function switch to ZERO and readjust the O_2 ZERO control to 0.00 if necessary. The meter is now ready to calibrate.

g. Calibration - Meters are calibrated using the Winkler azide method as described in this SOP in the Field Measurements Chapter III - section 3.2.

h. The D.O. probes are placed in a container of tap water with a relatively stable temperature. A minimum of four Winkler tests are then performed on the tap water. Three of the four resulting Winkler values must be within a 0.1 mg/l range. If the values are not in the 0.1 mg/l range, the Winkler tests should be repeated until the values are within the + or - 0.1 range. The three Winkler values are then averaged to provide an initial calibration value.

i. After the probes have stabilized in the container of tap water, the function switch is set to 0.01 mg/l, the meters are then adjusted to the initial calibration value by turning the O_2 CALIB control. The meters are now calibrated.

j. Leave the instrument on throughout the test to avoid re-polarizing the probe. Reactivate the stirrer approximately 2 minutes before each reading and turned off after the reading.

k. Obtain a bottom salinity reading using a YSI Model 33 S-C-T Meter. If salinity is present, the SALINITY knob on the YSI Model 58 D.O. Meter is adjusted accordingly.

l. Upon completion of the SOD test, perform a terminal calibration on all YSI 58 D.O. meters used. All terminal calibration data is recorded on the SOD terminal calibration form (Figure 23).

Note: If SOD tests are performed in coastal areas where tidal influence may cause salinity values to fluctuate during the test, salinity readings should be taken frequently and salinity adjustments made to the YSI 58 D.O. meters.

2.1.2 *TERMINAL CALIBRATION Method*

a. The D.O. probes are placed in a container of tap water with a relatively stable temperature and allowed to stabilize. A minimum of 4 Winkler tests are then performed on the tap water. The resulting Winkler values must be within a 0.1 mg/l range. If three of the four values are not in the 0.1 mg/l range, the Winkler tests should be repeated until the values are within the range. The Winkler values are then averaged to provide a terminal calibration value.

b. After the Winkler bottles have been filled with the tap water, turn on the stirrers, wait one minute and then record the D.O. and temperature readings.

c. Each D.O. reading should be within a 0.1 mg/l range from the average Winkler calibration value.

3. QUALITY ASSURANCE

3.1. Procedure

a. Complete the Pre-Sampling Calibration, Post-Sampling Calibration Check, and SOD Worksheets (Figure 23) on-site during each SOD test.

b. Perform Winkler tests per this SOP – Chapter III- section 3.1 – azide modification.

c. Perform a minimum of three Winkler titrations for Initial Calibration and Terminal Calibration.

d. Winkler values must be within a 0.1 mg/l range. If any value is outside the 0.1 mg/l range, then additional Winkler tests are performed until the values are within the range.

e. The terminal YSI 58 D.O. Meter reading should be within a 0.1 mg/l range from the average terminal Winkler calibration value.

f. A minimum ambient bottom D.O. of 2.0 mg/l is required to perform an SOD test (Murphy and Hicks, 1986).

g. Chamber velocities must be in a 0.08 to 0.12 ft/sec. range (Howard, 1988).
h. Take detailed field notes during the SOD test including a site description.
i. Conduct a pre-check to each SOD study to provide information on the study feasibility and station characteristics. During the -check sediment samples are generally collected to determine bottom characteristics.

Figure 23. Sediment Oxygen Demand Calibration Worksheet

SEDIMENT OXYGEN DEMAND CALIBRATION WORKSHEET

STUDY AREA	STATION
DATE	STAFF ON SITE

ALL METERS ZERO PRIOR TO CALIBRATION (YES NO)	CALIBRATION NOTES:
MEMBRANES VISUALLY CHECKED PRIOR TO CALIBRATION (YES NO)	
MEMBRANES LAST REPLACED	
BATTERIES LAST REPLACED	
CALIBRATOIN METHOD (SATURATED AIR WINKLER)	
CALIBRATION PERFORMED BY	
SALINITY	

INITIAL CALIBRATION

TIME OF INITIAL CALIBRATION
WINKLER READINGS: (A) (B) (C) (AVERAGE)

METER	AMB	BLANK O	BLANK OO	CLEAR	1	2	3	4	5	A	B	C
READINGS BEFORE CAL												
WINKLER												
DIFFERENCE												
ADJUSTED												

TERMINAL CALIBRATION

TIME OF INITIAL CALIBRATION
WINKLER READINGS: (A) (B) (C) (AVERAGE)

METER	AMB	BLANK O	BLANK OO	CLEAR	1	2	3	4	5	A	B	C
READINGS BEFORE CAL												
WINKLER												
DIFFERENCE												

4. CHAMBER DEPLOYMENT

After the D.O. meter calibration procedure is complete, the SOD chambers are prepared for the test. All chambers are prepared as follows prior to being placed into the water (Lawhorn, 1988).

4.1. Setting up Chambers

4.1.1. *Chamber Preparation*

a. Place the lids on replicate chambers in the up position with spacers located between the lid and lid companion ring. Wing nuts should be tight enough to hold the spacers in place but not so tight as to hamper removal after the chamber has been set in place on the bottom.

b. Insert the water sampling port stoppers on each chamber lid (size #1, two on each lid).

c. Open the monitoring probe port on all chamber lids (no stoppers).

d. Inspect the replicate chamber lid gaskets for damage or debris that could prevent a watertight seal.

e. Inspect the seals on the blank chambers for damage.

f. Clip the harness ropes to each chamber.

g. Open the water intake ports located on the bottom of the blank chambers (no stoppers).

h. Disconnect the return pump tubing from the chamber lid male connectors.

4.2. *Boat operation only:*

a. Hang the chambers in sequential order along the gunwale with the chamber lids several inches below the surface of the water.

b. Tie the chamber harness to a gunwale cleat.

c. Situate the boat over the bottom where the chambers will be placed.

d. Do not allow the chambers to disturb the bottom sediment.

4.3. *Land operation*:

Chambers are placed on the stream bank in the order that they will be deployed. This will prevent harness ropes, pump cables and probe cables from becoming tangled during the chamber deployment and the SOD test.

4.4. *Chamber deployment:*

a. Blank chambers are deployed first because sufficient time is required to replace surface water trapped inside the chamber with ambient bottom water prior to initiating the SOD test.

b. When deploying blank chambers in soft sediment, place the chambers in an area away from the area that the replicate chambers will be deployed in order to avoid stirred up sediments from being drawn into the chamber through the open probe port.

c. One clear polycarbonate and acrylic blank chamber is used in addition to the conventional aluminum blank chambers to provide an indication of whether or not photosynthesis is occurring in the water column. The mechanical functions and the deployment procedure for the clear blank chamber are identical to that of the aluminum blank chambers. In cases of high flow a weighted band should be placed around the clear chamber to prevent it from being washed away.

d. Each blank chamber must be filled with surface water that enters through the two filling ports located on the bottom plate of the chamber.

e. After the blank chamber is filled at the surface and prior to lowering the chamber, two #11½ stoppers must be inserted into the filling ports. Surface water is used to fill the blank chamber to create negative buoyancy so the chamber can be lowered to the bottom.

f. After the filling port stoppers are in place, the chamber is agitated to dislodge any air that is trapped under the lid. The trapped air will exit through the probe port.

g. The chamber is then lowered to the bottom.

h. When the blank chamber is on the bottom, the pump is turned on. Unlike the replicate chambers, the lid and bottom of the blank chambers are permanently sealed thus no water exchange occurs when the chamber is lowered to the bottom. Surface water must be purged from the chambers by operating the pump with the tubing disconnected from the male adapters on the lid while the chamber is on the bottom. Bottom water is drawn into the chamber through the open probe port while the surface water is purged through the disconnected return tubing. With the two return pump tubes disconnected, the chamber will purge surface water and draw in bottom water.

i. A light tapping on the pump housing and tubing will dislodge air bubbles trapped in the pump system.

j. The pump is then allowed to run while the other chambers are being deployed.

k. This procedure is repeated for each blank chamber.

4.5. *Replicate Chamber Deployment*

a. After the blank chambers are deployed, each replicate chamber is slowly lowered to the bottom substrate prior to setting the chamber.

b. Set the replicate chambers out in downstream to upstream order to prevent sediment disturbance and any silt that may have been disturbed from settling on areas where other chambers will be placed.

c. If the chamber location is unsatisfactory because of debris, or other bottom characteristics that would prevent the chamber from sealing then the chamber is carefully relocated. In addition, if the chamber location is atypical of the general stream area, the chamber or possibly the station should be relocated.

d. After the replicate chamber is placed in a satisfactory location on the bottom, carefully examine the sediment/flange seal and the sediment/inner core seal to assure that ambient water infiltration will not occur during the test.

e. The replicate chamber lid is then lowered by loosening the four wing nuts and removing the PVC spacers. The lid must be lowered very slowly as not to create a pressure wave and stir up silt inside the chamber. If silting occurs in the chamber, initial D.O. readings will be erratic and a longer period will be required for SOD rate stabilization (see: Section 5. Procedure for Recording SOD Data).

f. Replace the spacers between the companion ring and stainless steel washers. The wing nuts are then tightened and the gasket forms a watertight seal.

g. Activate the pump and lightly tap the pump housing and tubing to dislodge air trapped in the pump system.

h. Turn off the pump and allow any silt that may have been suspended to resettle before starting the test.

i. Reconnect the return tubing.

j. Repeat this process until all replicate chambers are deployed.

4.6. Once all replicate chambers are in place, insert DO probes into the probe ports beginning with the first blank chamber deployed and ending with the final replicate chamber.

4.7. During the D.O. probe installation, replicate chamber pumps can be turned on and a final check of the chamber and pump tubing can be performed.

4.8. In addition to the D.O. probes located inside the SOD chambers, one D.O. probe is placed on the outside of a chamber to record ambient D.O. values.

4.9. When an SOD test has been completed, chambers can usually be lifted from the bottom using the harness ropes.

5. RECORDING SOD FIELD DATA.

5.1. After SOD Chambers and Probes are installed

5.1.1 Readings

a. Stirrers are activated approximately 2 minutes prior to reading meters and turned off after the data is recorded.

b. All meters (including the ambient meter) are read at 15 minute intervals. For each chamber, D.O., temperature, and the change in D.O. per 15 minute time period is recorded on the SOD field sheet form (Figure 24).

c. D.O. readings from the replicate chambers will usually decrease at a relatively similar rate. Typically, if relatively uniform decreases in D.O. are observed in the replicate chambers after stabilization, a sufficient SOD rate can be calculated from approximately 2 hours of testing (Murphy and Hicks, 1986).

d. A minimum oxygen reduction of 0.4 mg/l is required before an SOD test should be terminated. This situation is not typically encountered and would provide an extremely low SOD rate indicating little organic content in the sediment.

e. SOD tests with very slow oxygen uptake rates may be less reliable due to an extremely small amount of oxygen depletion over a greater period of time. Since longer tests are necessary when slow oxygen uptake is occurring, the potential for meter calibration drift increases.

f. See Figure 25 for an example of completed SOD worksheet.

5.2 Recording Errors

5.2.1 *Erratic D.O. Readings Troubleshooting*

If observed in replicate chambers the following are possible problems:

a. Initial D.O. readings may be erratic if sediment was disturbed during chamber placement on the bottom. This problem occurs often at stations where sediment consists of soft mud or a silt-like composition and is usually observed in all of the replicate chambers. For this reason, several of the initial D.O. readings may be omitted from the SOD rate calculations. The readings will usually stabilize as the suspended particles in the chamber settle out, (generally about 15 to 30 minutes, 1 to 2 readings).

b. If D.O. readings from all chambers do not stabilize after 30 minutes, it may indicate that the chambers are sinking into the soft sediment causing the circulation diffusers to become close to the sediment and continually disturbing the silt. If this occurs, the chambers must be reset on the bottom and a chamber collar must be placed around the bottom chamber

flange to prevent the chambers from sinking. Chamber collars are flat, thin pieces of material, that increases the surface area of the chamber flange and prevent the chamber from sinking into soft sediment.

c. If D.O. readings from a replicate chamber do not stabilize and begin to decrease after the other chambers have stabilized, it may indicate that the chamber was not initially sealed and ambient bottom water is leaking into the chamber via the ports, gasket seal, pump tubes or the sediment flange seal. The chamber must be reset and the seal integrity reconfirmed.

d. On occasion, ambient water will begin leaking into a chamber. Chamber leaks (blowouts) are the most frequent problem encountered in SOD tests. This problem is easily recognized when D.O. values in a chamber that have been steadily decreasing suddenly begin to rise rapidly. However, if the chamber leak is small, the rate of decrease in D.O. may only be slowed, resulting in an unrealistically low rate for the chamber. For these reasons, the rate of D.O. change in each chamber must be carefully evaluated and recorded for each 15 minute time period during the SOD test.

   If a chamber leak is detected the following options may be considered:

   - Stop the leak and restart the test for that chamber; or
   - Delete the data from that chamber from the SOD test; or
   - Terminate entire test, if sufficient data has been recorded to establish a reliable linear regression.

e. If the D.O. in a chamber falls much more rapidly than in the other chambers, it may indicate that the chamber has been inadvertently placed on organic debris such as decaying leaves or other organically rich deposits that may be uncharacteristic of the area. The chambers must be placed on sediment that is typical for the station area. If this problem is encountered, the chamber should be relocated or the data deleted from the SOD test.

   The validity of SOD test data is dependent on locating the test site at an area that is typical of the water body being studied. If the chamber location is atypical of the general stream area then the chamber or possibly the station should be relocated.

f. When other obvious D.O. or temperature problems occur during the SOD test, it is usually the result of meter or probe malfunction and can be detected by the terminal calibration results.

6. METER AND PROBE PREPARATION

6.1. Procedure

a. Check all D.O. meters, cables and probes to assure proper functioning **before** the survey.

b. Evaluate the YSI 58 instrument batteries and replaced if necessary. Stirrer batteries should be checked to assure that batteries are adequate to complete SOD test.

c. Replace all D.O. probe membranes prior to each SOD survey. After the membrane has been changed, a minimum of 24 hours should be allowed for the probe to equilibrate before it is used for an SOD test. YSI Standard Membranes should be used.

7. SOD CHAMBER VELOCITY TEST

SOD rates are directly related to the sediment/water interface velocity, therefore specific and consistent velocities must be maintained in all chambers for accurate SOD testing. EPA recommends a constant chamber velocity of 0.1 ft/sec and an acceptable range of 0.08 to 0.12 ft/sec (Howard 1988). To maintain this velocity range, DWR uses a flow restrictor placed in the chamber pump tubing to reduce pumping velocity. The restrictor is 1" long, made from brass stock, and has a 7/64" opening in the center to allow a desired velocity of water.

All SOD chambers are periodically tested in the lab to ensure that velocities remain constant after repeated field use and pump wear. Velocity tests are performed using a Marsh McBirney Magnetic Flow Meter Model 201. The Marsh McBirney meter is factory calibrated. Chamber velocity tests procedures are as follows:

7.1. Velocity test procedures for replicate chambers:

a. Insert a # 11½ stopper in the monitoring probe port and two # 1 stoppers in water sampling ports. All pump tubing should be connected and the chamber lid must be tight against the chamber companion ring.

b. Place the chamber upside-down on a support in a manner that will allow access to the monitoring probe port. The support should not touch the pump tubing or alter the pump flow in any manner. (The chamber and support should be located over a sink or other acceptable area where the test water can be easily drained).

c. Fill the chamber with water to the cutting ring flange (normal water/sediment interface).

d. Turn the pump on. It may be necessary to add more water to fill pump and pump tubing after the pump is turned on and to tap the pump and tubing to dislodge trapped air. Place the Marsh McBirney probe 2 inches below the surface of the water halfway between the outer and inner chamber wall. Allow the

water circulation in the chamber to reach the maximum velocity (approximately 15 minutes).

e. Read the Marsh McBirney Meter. The velocity in the chamber should be within a range of 0.08 to 0.12 ft/sec.

f. If the velocity is not constant or out of the acceptable range, check the following:

- Probe orientation or placement in the chamber.
- Restrictions in pump tubing (7/64" brass restrictor may be blocked).
- Air bubbles could be locking the pump or altering flow.
- Pump may be damaged and not pumping maximum flow.
- Check pump battery voltage output (12 volt)
- Check velocity meter calibration.

7.2. Velocity Tests for Blank Chambers:

a. Insert two # 11½ stoppers into the filling ports on the bottom of the blank chamber. All pump tubing should be connected.

b. Place chamber right side up on a support in a manner that will allow access to the filling ports.

c. Fill the chamber completely with water.

d. Turn the pump on . It will be necessary to add more water to fill pump and pump tubing after the pump is turned on and to tap the pump and tubing to dislodge trapped air. Place the Marsh McBirney probe through the D.O. probe monitoring port at a depth of 2 inches. Allow the water circulation in the chamber to reach the maximum velocity (approximately 15 minutes).

e. Read the Marsh McBirney Meter.

f. Use the same trouble shooting procedures as with the replicate chambers if problems are encountered.

8. LEAK TEST FOR SOD CHAMBERS

SOD chambers must remain watertight during the SOD test to prevent ambient bottom water from entering the chamber and invalidating the test. The exchange of ambient bottom water and chamber water can occur by two means, by leaking between the sediment and chamber cutting edge or by leaking through any of the normally sealed chamber gaskets, stoppers, fittings and tube connections. Chamber leaks at the sediment/chamber interface generally occur as a result of sediment or sand washing out from around the chamber due to scouring and are usually detected during the test. Leaks through chamber seals, other than the sediment/chamber interface can be detected during the Chamber Velocity Test (Section 7). Note: leak test is under worst case conditions because chamber water (inside/outside) is equalized during the test. Procedures for leak testing SOD chambers are as follows:

1. Insert a # 11½ stopper in the monitoring probe port and # 1 stoppers in water sampling ports. All pump tubing should be connected and the chamber lid must be tight against the chamber companion ring.
2. Place the chamber upside-down on a support in a manner that will allow access to the monitoring probe port. The support should not touch the pump tubing or alter the pump flow in any manner. The chamber and support should be located over a sink or other acceptable area where the test water can be easily drained.
3. Fill the chamber with water to the cutting ring flange (normal water/sediment interface for replicate chambers and to bottom plate on blank chambers).
4. Turn the pump on.
5. If water leaks out, repair or replace the seal and repeat the leak test.

9. THREE POINT ANCHOR TECHNIQUE

If a boat operation is necessary to perform a SOD test, care must be taken to provide maximum stability and minimize wave action and horizontal swing over the bottom. Movement of the boat by wave action or swing on a single anchor line will result in chambers being lifted and the SOD test terminated. This problem can be avoided by using the following three-point anchor technique:

1. After the boat is on station, align the bow into the current.
2. Set bow anchor on SOD boat allowing a minimum scope of 3 times depth. More scope may be necessary if strong current or winds are present.
3. Use support boat to set aft port and aft starboard anchors (minimum scope 3 times depth).
4. Anchors should be oriented in a 3-point (tripod like) pattern with the SOD boat in the center.
5. After all anchors are set, the lines should be tightened as much as possible and cleated to provide maximum stability and minimize horizontal movement of the SOD boat.
6. While anchoring, care should be taken not to disturb the sediment where the SOD test is to be performed.
7. It is potentially dangerous to anchor with the stern of the boat facing upstream if current, waves or bad weather exists. The 3-point anchor method should not be used in areas affected by strong tidal current unless the test can be completed prior to the turning of the tide.

Figure 24. SOD Field Sheet

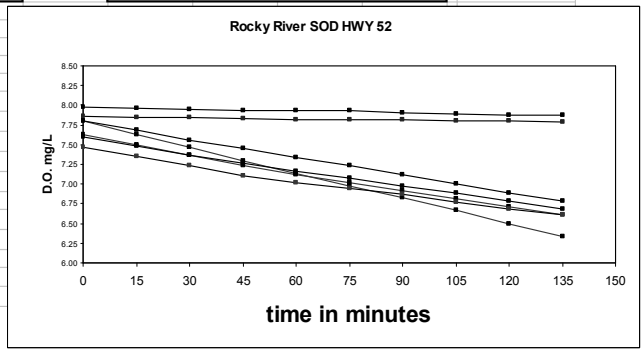
STUDY AREA																					
STATION LOCATION																					
DATE				SEDIMENT TYPE				DEPTH				CHAMBERS DIVER DEPLOYED? YES/NO				VELOCITY FT/SEC (at bottom)					
PERSON(S) READING METERS								STAFF ON SITE								BOAT SOD/BANK SOD					
TIME	MIN.	AMB		BLANK O		BLANK OO		BLANK CLEAR		REP 1		REP 2		REP 3		REP 4		REP 5		BACK-UP	
		DO	TEMP	DO	TEMP	DO	TEMP	DO	TEMP	DO	TEMP	DO	TEMP	DO	TEMP	DO	TEMP	DO	TEMP	DO	TEMP
	START																				
	15																				
	30																				
	45																				
	60																				
	75																				
	90																				
	105																				
	120																				
	135																				
	150																				
	165																				
	180																				
	195																				
	210																				
	225																				
	240																				
	255																				
	270																				

TIME	MIN.	Change in DO	Change in DO	Change in DO	Change in DO	Change in DO	Change in DO	Change in DO	Change in DO	Change in DO	Change in DO
	START										
	15										
	30										
	45										
	60										
	75										
	90										
	105										
	120										
	135										
	150										
	165										
	180										
	195										
	210										
	225										
	240										
	255										

XII. SEDIMENT OXYGEN DEMAND

Figure 25. Example of SOD Excel Worksheet for Determining Average SOD Rates.

Rocky River near Aquadale			STAFF ON SITE: QUIDLEY, WILLIAMS, FISHER, MEDLIN			TEST CONDUCTED FROM RIGHT BANK				
STATION LOCATION: Rocky River at Hwy 52			DEPTH AT SITE: 2 feet			AVERAGE AMBIENT WATER TEMP 24.4°C				
SUB-BASIN 03 07 13 COUNTY - Stanley			BOTTOM SEDIMENT: SAND			SOD TEST FOR SOD CALIBRATION				
		BLANK CHAMBERS			REPLICATE CHAMBERS					
	AMB	BLANK 0	BLANK OO		REP 1	REP 2	REP 3	REP 4	REP 5	Extra Chamber
NOTES										not used
AVERAGE T°C	24.3	24.3	24.4		24.4	24.3	24.4	24.3	24.4	
D.O. Range	7.81 - 8.02	7.79 - 7.86	7.87 - 7.97		6.34 - 7.80	6.61 - 7.63	6.78 - 7.80	6.69 - 7.60	6.61 - 7.47	
Test Time in min.										
0	7.99	7.86	7.97		7.80	7.63	7.80	7.60	7.47	
15	8.02	7.85	7.96		7.63	7.49	7.68	7.48	7.35	
30	8.00	7.84	7.95		7.47	7.37	7.56	7.37	7.23	
45	7.94	7.83	7.94		7.30	7.24	7.45	7.26	7.10	
60	7.83	7.82	7.93		7.14	7.12	7.34	7.17	7.02	
75	7.81	7.82	7.93		6.98	7.02	7.23	7.07	6.95	
90	7.90	7.81	7.91		6.83	6.91	7.12	6.98	6.87	
105	7.91	7.80	7.89		6.67	6.81	7.01	6.88	6.77	
120	7.93	7.80	7.88		6.50	6.71	6.89	6.78	6.68	
135	7.90	7.79	7.87		6.34	6.61	6.78	6.69	6.61	
RATE OF WATER COL (ß) mg/L/min		-0.0005	-0.0007							
RATE OF REPLICATE (ß) mg/L/min					-0.0108	-0.0073	-0.0075	-0.0067	-0.0063	
		-0.0006	AVG. RATE OF WATER COL (ß) mg/L/min		-0.0006	-0.0006	-0.0006	-0.0006	-0.0006	
RATE CALCULATION			REPLICATE RATE (-) AVG WATER COL RATE mg/L/min		-0.0102	-0.0067	-0.0069	-0.0061	-0.0057	
ß x (K x V) ÷ A = gr O2/m2/hr				SOD RATE gr/m2/hr	-0.1113	-0.0734	-0.0756	-0.0664	-0.0620	
ß = Rate of change in D.O.				gr/m2/day	-2.6713	-1.7624	-1.8147	-1.5937	-1.4884	
as mg O2/L/min										
v = Chamber volume in liters										
A = Chamber area in meters square										
K = .06 (Constant)		AVERAGE SEDIMENT OXYGEN DEMAND (rate calculated for 3 hours)								
		-0.0778 gr/m2/hr								
		-1.8661 gr/m2/day	AT AMB. TEMP 24.4°C			**-1.4145** CORRECTED TO 20°C (COEF 1.065)				
		-0.0072 gr/ft2/hr								
		-0.1734 gr/ft2/day								
FIELD STAFF :										
CALCULATIONS PERFORMED BY:										
Harold Quidley										
CALCULATIONS CHECKED BY:										
Ed Williams										



XII. SEDIMENT OXYGEN DEMAND

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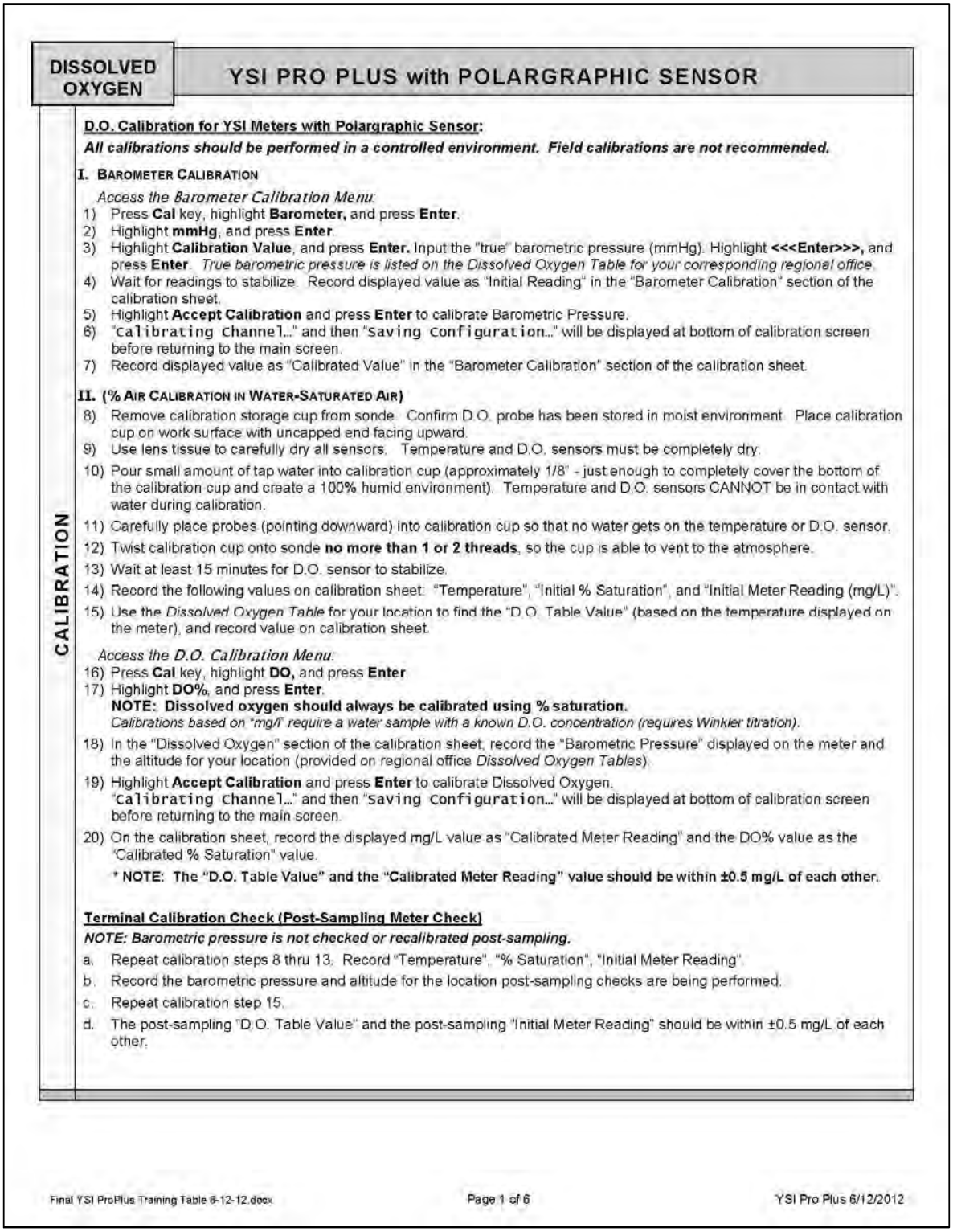
APPENDICES

Appendix 4: DWR's YSI Pro Plus Multiparameter Guidance Sheet



DISSOLVED OXYGEN

YSI PRO PLUS with POLARGRAPHIC SENSOR

CALIBRATION

D.O. Calibration for YSI Meters with Polargraphic Sensor:

All calibrations should be performed in a controlled environment. Field calibrations are not recommended.

I. BAROMETER CALIBRATION

Access the Barometer Calibration Menu:

1) Press **Cal** key, highlight **Barometer,** and press **Enter**.
2) Highlight **mmHg**, and press **Enter**.
3) Highlight **Calibration Value**, and press **Enter.** Input the "true" barometric pressure (mmHg). Highlight **<<<Enter>>>,** and press **Enter**. *True barometric pressure is listed on the Dissolved Oxygen Table for your corresponding regional office.*
4) Wait for readings to stabilize. Record displayed value as "Initial Reading" in the "Barometer Calibration" section of the calibration sheet.
5) Highlight **Accept Calibration** and press **Enter** to calibrate Barometric Pressure.
6) "`Calibrating Channel...`" and then "`Saving Configuration...`" will be displayed at bottom of calibration screen before returning to the main screen.
7) Record displayed value as "Calibrated Value" in the "Barometer Calibration" section of the calibration sheet.

II. (% AIR CALIBRATION IN WATER-SATURATED AIR)

8) Remove calibration storage cup from sonde. Confirm D.O. probe has been stored in moist environment. Place calibration cup on work surface with uncapped end facing upward.
9) Use lens tissue to carefully dry all sensors. Temperature and D.O. sensors must be completely dry.
10) Pour small amount of tap water into calibration cup (approximately 1/8" - just enough to completely cover the bottom of the calibration cup and create a 100% humid environment). Temperature and D.O. sensors CANNOT be in contact with water during calibration.
11) Carefully place probes (pointing downward) into calibration cup so that no water gets on the temperature or D.O. sensor.
12) Twist calibration cup onto sonde **no more than 1 or 2 threads**, so the cup is able to vent to the atmosphere.
13) Wait at least 15 minutes for D.O. sensor to stabilize.
14) Record the following values on calibration sheet: "Temperature", "Initial % Saturation", and "Initial Meter Reading (mg/L)".
15) Use the *Dissolved Oxygen Table* for your location to find the "D.O. Table Value" (based on the temperature displayed on the meter), and record value on calibration sheet.

Access the D.O. Calibration Menu:

16) Press **Cal** key, highlight **DO,** and press **Enter**.
17) Highlight **DO%**, and press **Enter**.
NOTE: Dissolved oxygen should always be calibrated using % saturation.
Calibrations based on "mg/l" require a water sample with a known D.O. concentration (requires Winkler titration).
18) In the "Dissolved Oxygen" section of the calibration sheet, record the "Barometric Pressure" displayed on the meter and the altitude for your location (provided on regional office *Dissolved Oxygen Tables*).
19) Highlight **Accept Calibration** and press **Enter** to calibrate Dissolved Oxygen.
"`Calibrating Channel...`" and then "`Saving Configuration...`" will be displayed at bottom of calibration screen before returning to the main screen.
20) On the calibration sheet, record the displayed mg/L value as "Calibrated Meter Reading" and the DO% value as the "Calibrated % Saturation" value.
*** NOTE: The "D.O. Table Value" and the "Calibrated Meter Reading" value should be within ±0.5 mg/L of each other.**

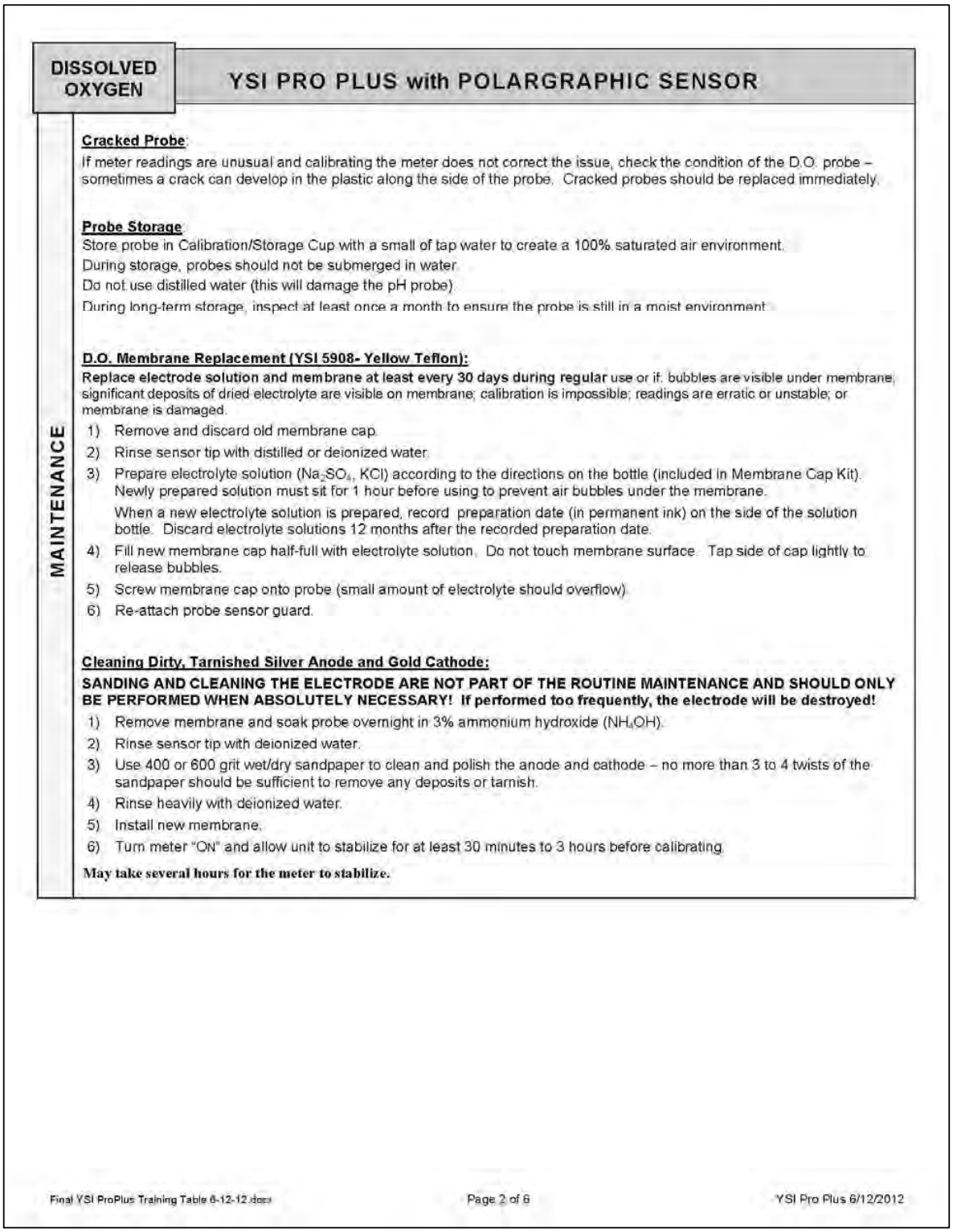
Terminal Calibration Check (Post-Sampling Meter Check)

NOTE: Barometric pressure is not checked or recalibrated post-sampling.

a. Repeat calibration steps 8 thru 13. Record "Temperature", "% Saturation", "Initial Meter Reading".
b. Record the barometric pressure and altitude for the location post-sampling checks are being performed.
c. Repeat calibration step 15.
d. The post-sampling "D.O. Table Value" and the post-sampling "Initial Meter Reading" should be within ±0.5 mg/L of each other.

Final YSI ProPlus Training Table 6-12-12.docx Page 1 of 6 YSI Pro Plus 6/12/2012

APPENDIX 4 – DWR GUIDANCE SHEET FOR YSI PROFESSIONAL PLUS METERS



DISSOLVED OXYGEN

YSI PRO PLUS with POLARGRAPHIC SENSOR

MAINTENANCE

Cracked Probe:

If meter readings are unusual and calibrating the meter does not correct the issue, check the condition of the D.O. probe – sometimes a crack can develop in the plastic along the side of the probe. Cracked probes should be replaced immediately.

Probe Storage:

Store probe in Calibration/Storage Cup with a small of tap water to create a 100% saturated air environment.

During storage, probes should not be submerged in water.

Do not use distilled water (this will damage the pH probe).

During long-term storage, inspect at least once a month to ensure the probe is still in a moist environment.

D.O. Membrane Replacement (YSI 5908- Yellow Teflon):

Replace electrode solution and membrane at least every 30 days during regular use or if: bubbles are visible under membrane; significant deposits of dried electrolyte are visible on membrane; calibration is impossible; readings are erratic or unstable; or membrane is damaged.

1) Remove and discard old membrane cap.
2) Rinse sensor tip with distilled or deionized water.
3) Prepare electrolyte solution (Na_2SO_4, KCl) according to the directions on the bottle (included in Membrane Cap Kit). Newly prepared solution must sit for 1 hour before using to prevent air bubbles under the membrane.

   When a new electrolyte solution is prepared, record preparation date (in permanent ink) on the side of the solution bottle. Discard electrolyte solutions 12 months after the recorded preparation date.
4) Fill new membrane cap half-full with electrolyte solution. Do not touch membrane surface. Tap side of cap lightly to release bubbles.
5) Screw membrane cap onto probe (small amount of electrolyte should overflow).
6) Re-attach probe sensor guard.

Cleaning Dirty, Tarnished Silver Anode and Gold Cathode:

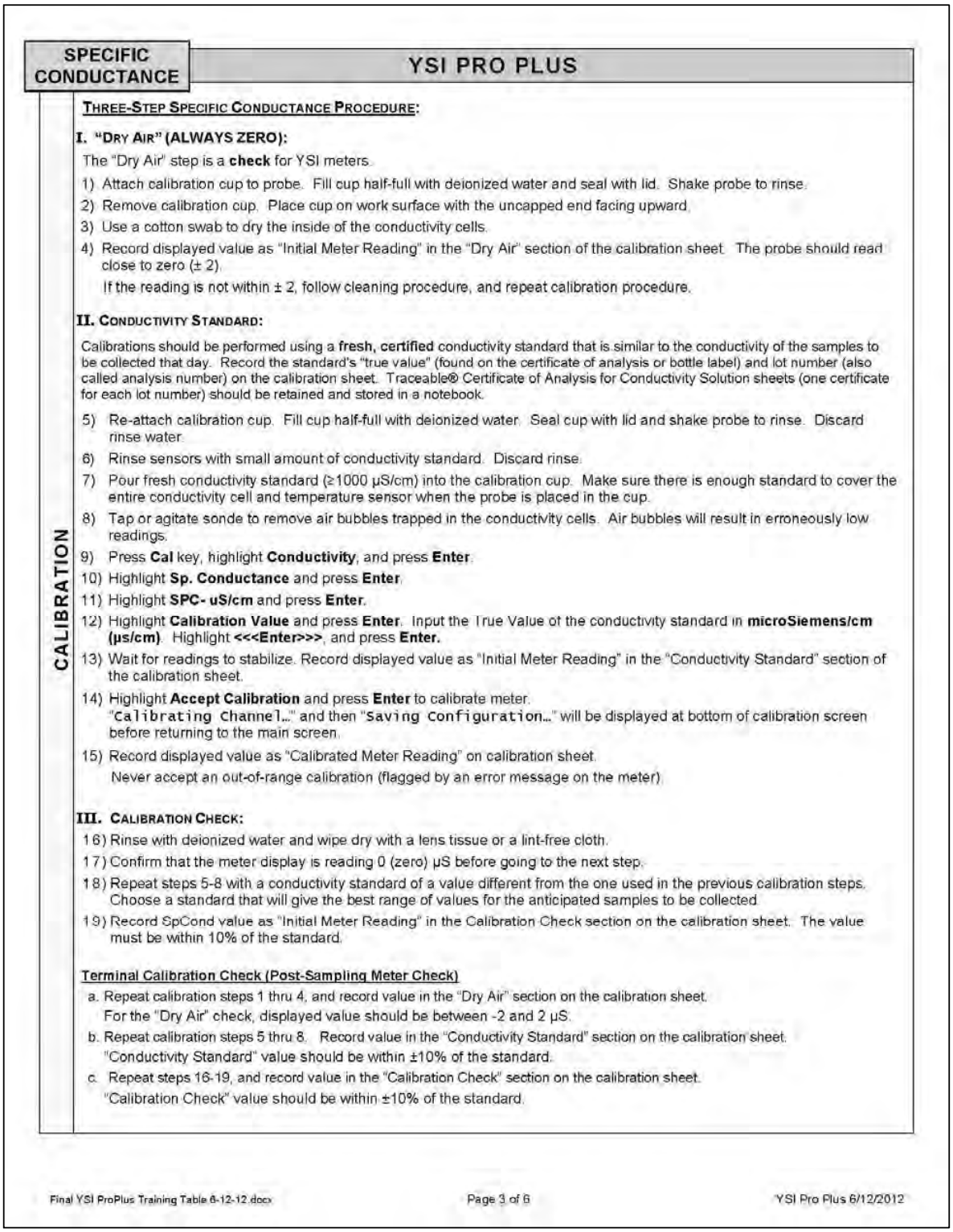
SANDING AND CLEANING THE ELECTRODE ARE NOT PART OF THE ROUTINE MAINTENANCE AND SHOULD ONLY BE PERFORMED WHEN ABSOLUTELY NECESSARY! If performed too frequently, the electrode will be destroyed!

1) Remove membrane and soak probe overnight in 3% ammonium hydroxide (NH_4OH).
2) Rinse sensor tip with deionized water.
3) Use 400 or 600 grit wet/dry sandpaper to clean and polish the anode and cathode – no more than 3 to 4 twists of the sandpaper should be sufficient to remove any deposits or tarnish.
4) Rinse heavily with deionized water.
5) Install new membrane.
6) Turn meter "ON" and allow unit to stabilize for at least 30 minutes to 3 hours before calibrating.

May take several hours for the meter to stabilize.

Final YSI ProPlus Training Table 6-12-12.docx Page 2 of 6 YSI Pro Plus 6/12/2012

APPENDIX 4 – DWR GUIDANCE SHEET FOR YSI PROFESSIONAL PLUS METERS



SPECIFIC CONDUCTANCE

YSI PRO PLUS

CALIBRATION

THREE-STEP SPECIFIC CONDUCTANCE PROCEDURE:

I. "DRY AIR" (ALWAYS ZERO):

The "Dry Air" step is a **check** for YSI meters.

1) Attach calibration cup to probe. Fill cup half-full with deionized water and seal with lid. Shake probe to rinse.
2) Remove calibration cup. Place cup on work surface with the uncapped end facing upward.
3) Use a cotton swab to dry the inside of the conductivity cells.
4) Record displayed value as "Initial Meter Reading" in the "Dry Air" section of the calibration sheet. The probe should read close to zero (± 2).
   If the reading is not within ± 2, follow cleaning procedure, and repeat calibration procedure.

II. CONDUCTIVITY STANDARD:

Calibrations should be performed using a **fresh, certified** conductivity standard that is similar to the conductivity of the samples to be collected that day. Record the standard's "true value" (found on the certificate of analysis or bottle label) and lot number (also called analysis number) on the calibration sheet. Traceable® Certificate of Analysis for Conductivity Solution sheets (one certificate for each lot number) should be retained and stored in a notebook.

5) Re-attach calibration cup. Fill cup half-full with deionized water. Seal cup with lid and shake probe to rinse. Discard rinse water.
6) Rinse sensors with small amount of conductivity standard. Discard rinse.
7) Pour fresh conductivity standard (≥1000 µS/cm) into the calibration cup. Make sure there is enough standard to cover the entire conductivity cell and temperature sensor when the probe is placed in the cup.
8) Tap or agitate sonde to remove air bubbles trapped in the conductivity cells. Air bubbles will result in erroneously low readings.
9) Press **Cal** key, highlight **Conductivity**, and press **Enter**.
10) Highlight **Sp. Conductance** and press **Enter**.
11) Highlight **SPC- uS/cm** and press **Enter.**
12) Highlight **Calibration Value** and press **Enter**. Input the True Value of the conductivity standard in **microSiemens/cm (µs/cm)**. Highlight **<<<Enter>>>**, and press **Enter.**
13) Wait for readings to stabilize. Record displayed value as "Initial Meter Reading" in the "Conductivity Standard" section of the calibration sheet.
14) Highlight **Accept Calibration** and press **Enter** to calibrate meter.
    "`Calibrating Channel…`" and then "`Saving Configuration…`" will be displayed at bottom of calibration screen before returning to the main screen.
15) Record displayed value as "Calibrated Meter Reading" on calibration sheet.
    Never accept an out-of-range calibration (flagged by an error message on the meter).

III. CALIBRATION CHECK:

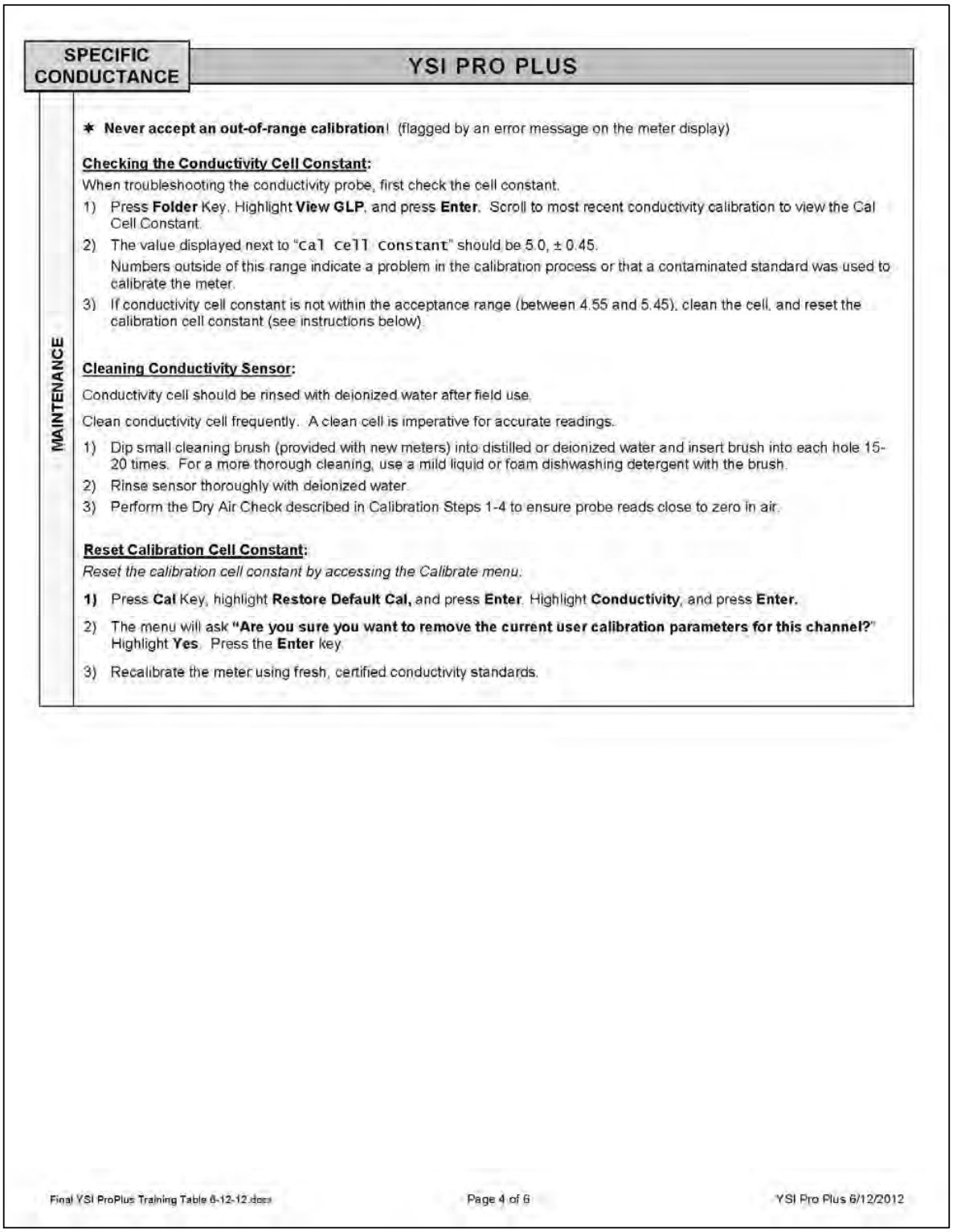
16) Rinse with deionized water and wipe dry with a lens tissue or a lint-free cloth.
17) Confirm that the meter display is reading 0 (zero) µS before going to the next step.
18) Repeat steps 5-8 with a conductivity standard of a value different from the one used in the previous calibration steps. Choose a standard that will give the best range of values for the anticipated samples to be collected.
19) Record SpCond value as "Initial Meter Reading" in the Calibration Check section on the calibration sheet. The value must be within 10% of the standard.

Terminal Calibration Check (Post-Sampling Meter Check)

a. Repeat calibration steps 1 thru 4, and record value in the "Dry Air" section on the calibration sheet.
   For the "Dry Air" check, displayed value should be between -2 and 2 µS.
b. Repeat calibration steps 5 thru 8. Record value in the "Conductivity Standard" section on the calibration sheet.
   "Conductivity Standard" value should be within ±10% of the standard.
c. Repeat steps 16-19, and record value in the "Calibration Check" section on the calibration sheet.
   "Calibration Check" value should be within ±10% of the standard.

Final YSI ProPlus Training Table 6-12-12.docx Page 3 of 6 YSI Pro Plus 6/12/2012

APPENDIX 4 – DWR GUIDANCE SHEET FOR YSI PROFESSIONAL PLUS METERS



SPECIFIC CONDUCTANCE

YSI PRO PLUS

MAINTENANCE

* **Never accept an out-of-range calibration**! (flagged by an error message on the meter display)

Checking the Conductivity Cell Constant:

When troubleshooting the conductivity probe, first check the cell constant.

1) Press **Folder** Key. Highlight **View GLP**, and press **Enter**. Scroll to most recent conductivity calibration to view the Cal Cell Constant.
2) The value displayed next to "`Cal Cell Constant`" should be 5.0, ± 0.45.
   Numbers outside of this range indicate a problem in the calibration process or that a contaminated standard was used to calibrate the meter.
3) If conductivity cell constant is not within the acceptance range (between 4.55 and 5.45), clean the cell, and reset the calibration cell constant (see instructions below).

Cleaning Conductivity Sensor:

Conductivity cell should be rinsed with deionized water after field use.

Clean conductivity cell frequently. A clean cell is imperative for accurate readings.

1) Dip small cleaning brush (provided with new meters) into distilled or deionized water and insert brush into each hole 15-20 times. For a more thorough cleaning, use a mild liquid or foam dishwashing detergent with the brush.
2) Rinse sensor thoroughly with deionized water.
3) Perform the Dry Air Check described in Calibration Steps 1-4 to ensure probe reads close to zero in air.

Reset Calibration Cell Constant:

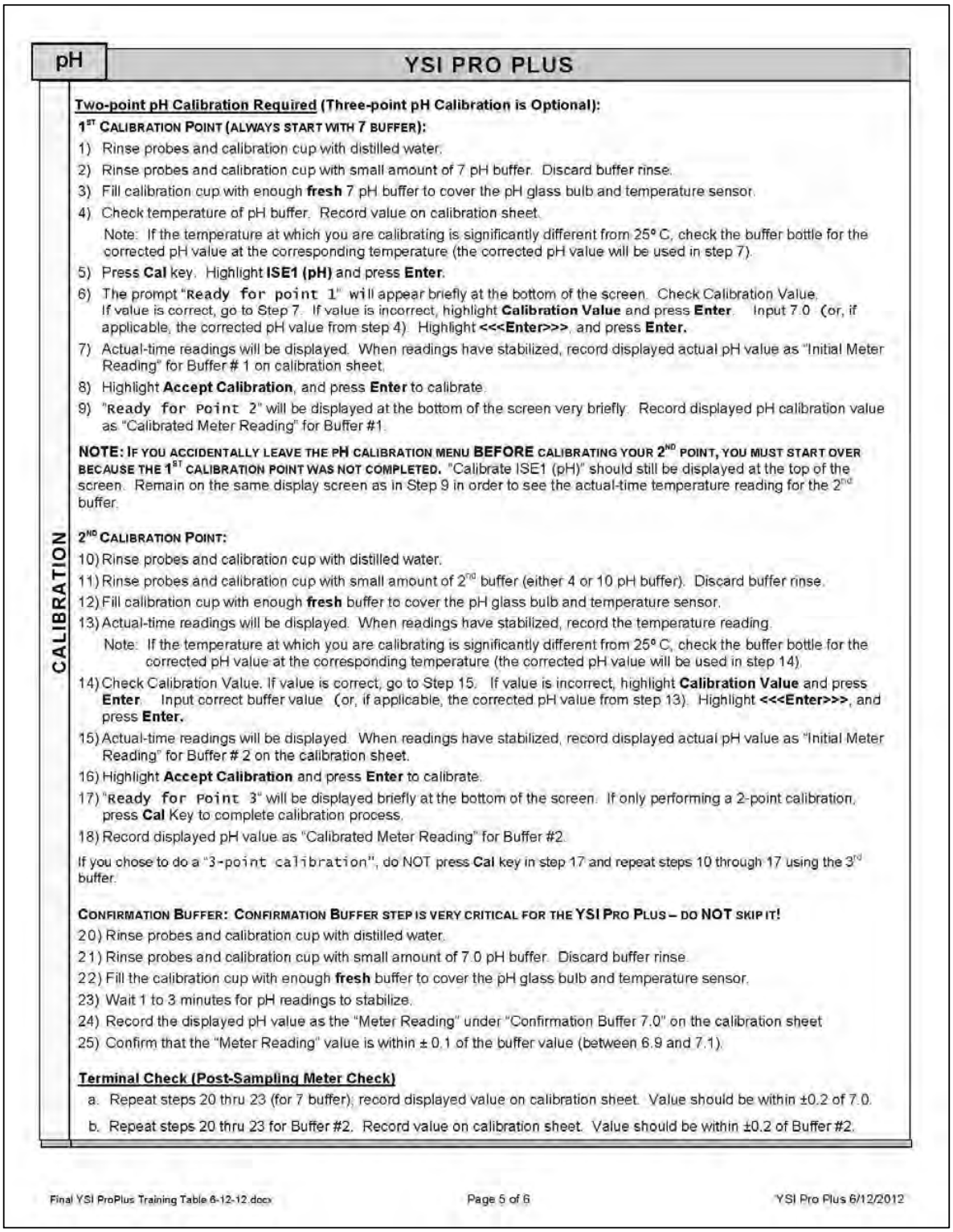
Reset the calibration cell constant by accessing the Calibrate menu.

1) Press **Cal** Key, highlight **Restore Default Cal,** and press **Enter**. Highlight **Conductivity**, and press **Enter.**

2) The menu will ask **"Are you sure you want to remove the current user calibration parameters for this channel?"** Highlight **Yes**. Press the **Enter** key.

3) Recalibrate the meter using fresh, certified conductivity standards.

Final YSI ProPlus Training Table 6-12-12.docx Page 4 of 6 YSI Pro Plus 6/12/2012



pH

YSI PRO PLUS

CALIBRATION

Two-point pH Calibration Required (Three-point pH Calibration is Optional):

1ST CALIBRATION POINT (ALWAYS START WITH 7 BUFFER):

1) Rinse probes and calibration cup with distilled water.
2) Rinse probes and calibration cup with small amount of 7 pH buffer. Discard buffer rinse.
3) Fill calibration cup with enough **fresh** 7 pH buffer to cover the pH glass bulb and temperature sensor.
4) Check temperature of pH buffer. Record value on calibration sheet.
   Note: If the temperature at which you are calibrating is significantly different from 25° C, check the buffer bottle for the corrected pH value at the corresponding temperature (the corrected pH value will be used in step 7).
5) Press **Cal** key. Highlight **ISE1 (pH)** and press **Enter**.
6) The prompt "`Ready for point 1`" will appear briefly at the bottom of the screen. Check Calibration Value. If value is correct, go to Step 7. If value is incorrect, highlight **Calibration Value** and press **Enter**. Input 7.0 (or, if applicable, the corrected pH value from step 4). Highlight **<<<Enter>>>**, and press **Enter.**
7) Actual-time readings will be displayed. When readings have stabilized, record displayed actual pH value as "Initial Meter Reading" for Buffer # 1 on calibration sheet.
8) Highlight **Accept Calibration**, and press **Enter** to calibrate.
9) "`Ready for Point 2`" will be displayed at the bottom of the screen very briefly. Record displayed pH calibration value as "Calibrated Meter Reading" for Buffer #1.

NOTE: IF YOU ACCIDENTALLY LEAVE THE PH CALIBRATION MENU BEFORE CALIBRATING YOUR 2ND POINT, YOU MUST START OVER BECAUSE THE 1ST CALIBRATION POINT WAS NOT COMPLETED. "Calibrate ISE1 (pH)" should still be displayed at the top of the screen. Remain on the same display screen as in Step 9 in order to see the actual-time temperature reading for the 2nd buffer.

2ND CALIBRATION POINT:

10) Rinse probes and calibration cup with distilled water.
11) Rinse probes and calibration cup with small amount of 2nd buffer (either 4 or 10 pH buffer). Discard buffer rinse.
12) Fill calibration cup with enough **fresh** buffer to cover the pH glass bulb and temperature sensor.
13) Actual-time readings will be displayed. When readings have stabilized, record the temperature reading.
    Note: If the temperature at which you are calibrating is significantly different from 25° C, check the buffer bottle for the corrected pH value at the corresponding temperature (the corrected pH value will be used in step 14).
14) Check Calibration Value. If value is correct, go to Step 15. If value is incorrect, highlight **Calibration Value** and press **Enter**. Input correct buffer value (or, if applicable, the corrected pH value from step 13). Highlight **<<<Enter>>>**, and press **Enter.**
15) Actual-time readings will be displayed. When readings have stabilized, record displayed actual pH value as "Initial Meter Reading" for Buffer # 2 on the calibration sheet.
16) Highlight **Accept Calibration** and press **Enter** to calibrate.
17) "`Ready for Point 3`" will be displayed briefly at the bottom of the screen. If only performing a 2-point calibration, press **Cal** Key to complete calibration process.
18) Record displayed pH value as "Calibrated Meter Reading" for Buffer #2.

If you chose to do a "`3-point calibration`", do NOT press **Cal** key in step 17 and repeat steps 10 through 17 using the 3rd buffer.

CONFIRMATION BUFFER: CONFIRMATION BUFFER STEP IS VERY CRITICAL FOR THE YSI PRO PLUS – DO NOT SKIP IT!

20) Rinse probes and calibration cup with distilled water.
21) Rinse probes and calibration cup with small amount of 7.0 pH buffer. Discard buffer rinse.
22) Fill the calibration cup with enough **fresh** buffer to cover the pH glass bulb and temperature sensor.
23) Wait 1 to 3 minutes for pH readings to stabilize.
24) Record the displayed pH value as the "Meter Reading" under "Confirmation Buffer 7.0" on the calibration sheet
25) Confirm that the "Meter Reading" value is within ± 0.1 of the buffer value (between 6.9 and 7.1).

Terminal Check (Post-Sampling Meter Check)

a. Repeat steps 20 thru 23 (for 7 buffer), record displayed value on calibration sheet. Value should be within ±0.2 of 7.0.
b. Repeat steps 20 thru 23 for Buffer #2. Record value on calibration sheet. Value should be within ±0.2 of Buffer #2.

Final YSI ProPlus Training Table 6-12-12.docx Page 5 of 6 YSI Pro Plus 6/12/2012

APPENDIX 4 – DWR GUIDANCE SHEET FOR YSI PROFESSIONAL PLUS METERS

pH — **YSI PRO PLUS**

MAINTENANCE

* **Never accept an out-of-range calibration**! (flagged by an error message on the meter display)

Indicators that maintenance is needed:
Difficulty calibrating pH sensor, slow response, erratic readings, clogged or black reference junction, coated glass bulb.

Probe Storage:

Do NOT allow the pH sensor to dry out! Sensors that have dried out may be permanently damaged!

Store probe in calibration/storage cup filled with 1/8" of tap water (never use distilled water to store probe).

If probe will not be used for several months, remove probe and store in pH 4 buffer. Seal the vacant port with a port plug.

Probe Lifespan:

The pH probe has a lifetime of approximately 12-24 months (in some cases, probes may last 3+ years).

When troubleshooting pH sensor problems, start by checking age of probe and replace as-needed.

On the side of each probe is the imprint "YSI 1001" followed by 2 numbers and a letter. The 2 numbers and the letter indicate the year and month in which the probe was made. For instance, 07D means the probe was made in April, 2007. (i.e. A=Jan, B=Feb, etc.).

Troubleshooting with mV readings:

1) Follow steps for pH calibration. During calibration, record pH mV values from the "Calibrated" screen for each buffer.
2) Evaluate the pH mV values:
   The span or "slope" between the pH 4 and pH 7 and between pH 7 and pH 10 should be approximately 165 to 180 mV.
   pH 7 should be 0 mV ± 50 mV. pH 4 should be 180 mV ± 50 mV. pH 10 should be -180 mV ± 50 mV.
   Example: If a probe reads +10 mV in pH 7 buffer, then the probe should also read between 175 and 190 mV in pH 4 buffer, and between -155 mV and -170mV in pH 10 buffer.
3) If the mV values fall outside the range of 160-180 mV, the probe should be replaced soon.
   Note: The probe will no longer calibrate when the span is outside of the range of 150-210 mV.

General pH Probe Cleaning:

Use deionized water and a soft lens cloth or a cotton swab to remove foreign material from the glass bulb. If good response is not restored, perform the following procedure:

1) GENTLY clean the glass bulb and white probe face by carefully rubbing a cotton swab soaked in mild dishwashing detergent. Apply little to no pressure, as the glass bulb is very thin and fragile!
2) Rinse probe thoroughly with deionized water.
3) Wipe probe with cotton swab that has been saturated with water. Rinse probe again.

Advanced pH Probe Cleaning and Restoration:

The need and frequency depend on the type of surface water being monitoring.

The probe must be removed from the sonde before advanced cleaning.

To remove more resistant deposits and biological growth, use HCl acid and bleach.

To perform an advanced cleaning, refer to the Care, Maintenance, and Storage section of the YSI Professional Plus User Manual.

Reference Junction:

The reference junction is a small tab located between the edge of the white surface of the pH probe face and the gray raised area around the pH probe face.

When new, the junction will be an off-white color.

As it ages, the junction will become darker.

A black reference junction coupled with slow response and/or erratic readings indicates a more advanced cleaning may be needed.

Final YSI ProPlus Training Table 6-12-12.docx Page 6 of 6 YSI Pro Plus 6/12/2012

APPENDIX 5: Uncorrected Dissolved Oxygen Table

Corrected D.O. Tables for a specific location or DWR office are available upon request from the ESS

Sea Level *(Uncorrected D.O. Values)*

Dissolved Oxygen (D.O.) TABLE

Altitude at Sea Level = 0 feet

Barometric Pressure (BP) at Sea Level = 760 mm Hg

Temp (°C)	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	Temp (°C)
0	14.6	14.6	14.5	14.5	14.5	14.4	14.4	14.3	14.3	14.3	0
1	14.2	14.2	14.1	14.1	14.1	14.0	14.0	13.9	13.9	13.9	1
2	13.8	13.8	13.8	13.7	13.7	13.6	13.6	13.6	13.5	13.5	2
3	13.5	13.4	13.4	13.4	13.3	13.3	13.2	13.2	13.2	13.1	3
4	13.1	13.1	13.0	13.0	13.0	12.9	12.9	12.9	12.8	12.8	4
5	12.8	12.7	12.7	12.7	12.6	12.6	12.6	12.5	12.5	12.5	5
6	12.4	12.4	12.4	12.4	12.3	12.3	12.3	12.2	12.2	12.2	6
7	12.1	12.1	12.1	12.0	12.0	12.0	12.0	11.9	11.9	11.9	7
8	11.8	11.8	11.8	11.8	11.7	11.7	11.7	11.6	11.6	11.6	8
9	11.6	11.5	11.5	11.5	11.4	11.4	11.4	11.4	11.3	11.3	9
10	11.3	11.3	11.2	11.2	11.2	11.2	11.1	11.1	11.1	11.1	10
11	11.0	11.0	11.0	11.0	10.9	10.9	10.9	10.9	10.8	10.8	11
12	10.8	10.8	10.7	10.7	10.7	10.7	10.6	10.6	10.6	10.6	12
13	10.5	10.5	10.5	10.5	10.4	10.4	10.4	10.4	10.4	10.3	13
14	10.3	10.3	10.3	10.2	10.2	10.2	10.2	10.1	10.1	10.1	14
15	10.1	10.1	10.0	10.0	10.0	10.0	10.0	9.9	9.9	9.9	15
16	9.9	9.8	9.8	9.8	9.8	9.8	9.7	9.7	9.7	9.7	16
17	9.7	9.6	9.6	9.6	9.6	9.6	9.5	9.5	9.5	9.5	17
18	9.5	9.4	9.4	9.4	9.4	9.4	9.4	9.3	9.3	9.3	18
19	9.3	9.3	9.2	9.2	9.2	9.2	9.2	9.1	9.1	9.1	19
20	9.1	9.1	9.1	9.0	9.0	9.0	9.0	8.97	8.9	8.9	20
21	8.9	8.9	8.9	8.9	8.8	8.8	8.8	8.8	8.8	8.8	21
22	8.7	8.7	8.7	8.7	8.7	8.7	8.6	8.6	8.6	8.6	22
23	8.6	8.6	8.5	8.5	8.5	8.5	8.5	8.5	8.4	8.4	23
24	8.4	8.4	8.4	8.4	8.4	8.3	8.3	8.3	8.3	8.3	24
25	8.3	8.2	8.2	8.2	8.2	8.2	8.2	8.2	8.1	8.1	25
26	8.1	8.1	8.1	8.1	8.1	8.0	8.0	8.0	8.0	8.0	26
27	8.0	8.0	7.9	7.9	7.9	7.9	7.9	7.9	7.9	7.8	27
28	7.8	7.8	7.8	7.8	7.8	7.8	7.7	7.7	7.7	7.7	28
29	7.7	7.7	7.7	7.7	7.6	7.6	7.6	7.6	7.6	7.6	29
30	7.6	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.4	30
31	7.4	7.4	7.4	7.4	7.4	7.4	7.4	7.3	7.3	7.3	31
32	7.3	7.3	7.3	7.3	7.3	7.2	7.2	7.2	7.2	7.2	32
33	7.2	7.2	7.2	7.1	7.1	7.1	7.1	7.1	7.1	7.1	33
34	7.1	7.1	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	34
35	6.9	6.9	6.9	6.9	6.9	6.9	6.9	6.9	6.9	6.8	35

* All D.O. values are in mg/L

Uncorrected Table **08/24/2007**

APPENDIX 5 – UNCORRECTED DISSOLVED OXYGEN TABLE

D.O. Correction Chart

Altitude (ft)	Barometric Pressure (mmHg)	Correction Factor	Altitude (ft)	Barometric Pressure (mmHg)	Correction Factor
100	757	0.996	2400	695	0.914
200	755	0.993	2500	692	0.910
300	752	0.989	2600	689	0.907
400	749	0.985	2700	686	0.903
500	746	0.981	2800	684	0.900
600	743	0.978	2900	682	0.897
700	740	0.974	3000	679	0.893
800	737	0.970	3100	676	0.890
900	735	0.967	3200	673	0.886
1000	732	0.963	3300	671	0.883
1100	729	0.959	3400	669	0.880
1200	727	0.956	3500	666	0.876
1300	724	0.952	3600	663	0.873
1400	721	0.949	3700	661	0.870
1500	718	0.945	3800	658	0.866
1600	715	0.941	3900	656	0.863
1700	713	0.938	4000	654	0.860
1800	710	0.934	4100	651	0.857
1900	708	0.931	4200	648	0.853
2000	705	0.927	4300	646	0.850
2100	702	0.924	4400	644	0.847
2200	699	0.920	4500	641	0.844
2300	697	0.917			

How to Correct D.O. Table Values:

Corrected D.O. Value = Value from Sea Level Table x Correction Factor

1) Use the temperature displayed on your meter and the "Sea Level Table" (on the back of this page) to find the *Uncorrected D.O. Value*.

2) Use your location's altitude and the "D.O. Correction Chart" (on this page) to find the corresponding *Correction Factor*.

3) Multiply the *Uncorrected D.O. Value* (from step 1) by the *Correction Factor* (from step 2) to get the *Corrected D.O. Value*.

4) The value calculated in step 3 (*Corrected D.O. Value*) and the value displayed on the meter should be within ± 0.5 mg/L of each other.

Corrected D.O. Tables for a specific location or DWR office are available upon request from the ESS QA Coordinator.

D.O. Correction Factors

08/24/2007

APPENDIX 5 – UNCORRECTED DISSOLVED OXYGEN TABLE

APPENDIX 6: SOP for Filtering in the Field

STANDARD OPERATING PROCEDURES FOR FIELD FILTERING USING THE VACUUM PUMP PROCEDURE.

Field Procedure:

1. Obtain filtering equipment including sterile 0.45 µm 47 mm diameter Millipore filters, glass fiber filters, nitrile gloves, forceps, and a supply of deionized (DI) water. An example of an appropriate filtering kit is Nalgene - filter holder with receiver 500 mL (Nalgene #300-4050).
2. After donning gloves, thoroughly rinse the field filtering equipment with deionized water on the day of sampling at the first sampling station.
3. Remove 0.45 um filter from package with clean forceps and place on the filter platform, gridded side up.
4. Inspect filter for proper placement-centered; no wrinkles, bends, cracks, holes, or gaps.
5. Reassemble apparatus.
6. Attach hand pump to outlet of bottom chamber with tubing.
7. If first sample of the day, do field blank for quality control first using DI water and following steps 8-16.
8. Pour required volume of sample water in the top chamber (example-volume for orthophosphorus and dissolved phosphorus is at least 200 mL for each).
9. Use hand pump to create vacuum.
10. Continue adding sample and pumping until required filtered volume (based on parameter) is obtained and top chamber is empty. **Note:** It may be necessary to change filters several times or use a glass fiber pre-filter (see turbid samples options below) to obtain enough filtrate.
11. Samples for all dissolved parameters can be filtered at once.
12. Before disassembling, make sure that no sample remains in the top chamber and no pressure in the bottom chamber: remove tubing, or press release on pump.
13. Disassemble apparatus.
14. Decant filtrate into sample bottles, preserve and handle as per laboratory guidance.
15. Remove filter with forceps and dispose of filter.
16. Rinse filtering apparatus with DI water. This rinse must be repeated before field filtering at any additional locations (i.e. between stations).
17. After last sample of the day is completed, do terminal field blank sample.

Turbid Samples Options:

When the filter becomes clogged:

Option 1: Change filters

1. Finish filtering any sample left in top chamber.
2. Ensure zero pressure in bottom chamber.
3. Disassemble apparatus.
4. Using forceps, remove clogged filter and replace with new filter. **Caution:** Don't let residue on filter contact any part of the interior of the apparatus or tips of forceps.
5. Re-assemble apparatus and continue filtering.

Field Filtering SOP (Cont.)

Option 2: Pre-filter

1. The sample can be taken through a preliminary step using a filter with a larger pore size, such as a glass fiber filter.
2. This can be accomplished by placing the glass fiber filter on top of the 0.45 *u*m filter on the filter platform. A small amount of DI water can be squirted on top of the combined filters to prevent vapor lock. It may be necessary to change these filters as they get clogged to obtain enough filtrate but this procedure should minimize the number of times the filters must be changed.

Quality Control Procedures

1. The filtering apparatus and DI wash bottle should be regularly cleaned with phosphate-free detergent and completely rinsed with DI water, as is done with all other sampling equipment.
2. Initial and terminal quality control samples (blanks) of filtered deionized water must be taken for each day's sampling for each parameter and submitted to the laboratory.
3. Blanks must be filtered in the field: one at the beginning of the day before the first water sample is processed, and one at the end of the day after the last water sample is processed.
4. Sources of contamination include:
   -air/environment;
   -field staff;
   -sampling equipment and bottle;
   -filtration equipment (filter holder, filter, tubing);
   -DI water, and
   -chemical preservatives.
5. Station location on the lab sheet should indicate QC sample type.
6. Blanks should come back as non-detects.
7. If blanks show detectable levels of analytes:
   - results from associated samples must be flagged, and flags reported to data users.
   - perform rigorous data review to see if contamination concerns are severe enough to warrant discarding the data.
   - patterns of dirty blanks should be reviewed and a plan for contamination source identification, corrective actions, and re-evaluations should be developed.

APPENDIX 7: Flow Measurement Field Sheet

Flow Sheet

Location: ______________________________

Station: ______________________________

Date: ____________ Time: ____________

Staff: ______________________________

	Distance (ft.)	Depth (ft.)	Velocity (fps)		Notes:
RB		-------	----------		

****need a minimum of 18 points

***depths of 2.5 feet and less, the average velocity is measured at 0.6 of the depth from the water surface.

*** depths greater than 2.5 feet measure the velocity at 0.2 and 0.8 of the water depth (the average of these two velocities will later be recorded as a single value).

METHOD 415.3 DETERMINATION OF TOTAL ORGANIC CARBON AND SPECIFIC UV ABSORBANCE AT 254 nm IN SOURCE WATER AND DRINKING WATER

Revision 1.2
September, 2009

B. B. Potter, USEPA, Office of Research and Development, National Exposure Research Laboratory
J. C. Wimsatt, The National Council On The Aging, Senior Environmental Employment Program

NATIONAL EXPOSURE RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

415.3 - 1

METHOD 415.3
DETERMINATION OF TOTAL ORGANIC CARBON AND SPECIFIC UV ABSORBANCE AT 254 nm IN SOURCE WATER AND DRINKING WATER

1.0 SCOPE AND APPLICATION

1.1 This method provides procedures for the determination of total organic carbon (TOC), dissolved organic carbon (DOC), and UV absorption at 254 nm (UVA) in source waters and drinking waters. The DOC and UVA determinations are used in the calculation of the Specific UV Absorbance (SUVA). For TOC and DOC analysis, the sample is acidified and the inorganic carbon (IC) is removed prior to analysis for organic carbon (OC) content using a TOC instrument system. The measurements of TOC and DOC are based on calibration with potassium hydrogen phthalate (KHP) standards. This method is not intended for use in the analysis of treated or untreated industrial wastewater discharges as those wastewater samples may damage or contaminate the instrument system(s).

1.2 The three (3) day, pooled organic carbon detection limit (OCDL) is based on the detection limit (DL) calculation.[1] It is a statistical determination of precision, and may be below the level of quantitation. The determination of OCDL is dependent on the analytical instrument system's precision, the purity of laboratory reagent water (LRW), and the skill of the analyst. Different TOC instrument systems have produced significantly different OCDLs that range between 0.02 and 0.12 mg/L OC for both TOC and DOC measurements. Examples of these data can be seen in Section 17, Table 17.1. It should be noted that background levels of OC contamination are problematic. The minimum reporting level (MRL) for TOC and DOC will depend on the laboratory's ability to control background levels (Sect. 4).

2.0 SUMMARY OF METHOD

2.1 In both TOC and DOC determinations, organic carbon in the water sample is oxidized to produce carbon dioxide (CO_2), which is then measured by a detection system. There are two different approaches for the oxidation of organic carbon in water samples to carbon dioxide gas: (a) combustion in an oxidizing gas and (b) UV promoted or heat catalyzed chemical oxidation with a persulfate solution. Carbon dioxide, which is released from the oxidized sample, is detected by a conductivity detector or by a nondispersive infrared (NDIR) detector. Instruments using any combination of the above technologies may be used in this method.

2.2 Settleable solids and floating matter may cause plugging of valves, tubing, and the injection needle and/or injection port. The TOC procedure allows the removal of settleable solids and floating matter. The suspended matter is considered part of the

sample. The resulting water sample is then considered a close approximation of the original whole water sample for the purpose of TOC measurement.

2.3 The DOC procedure requires that the sample be passed through a 0.45-µm filter prior to analysis to remove particulate OC from the sample.

2.4 The TOC and DOC procedures require that all IC be removed from the sample before the sample is analyzed for organic carbon content. If the IC is not completely removed, **significant error will occur.** The sample, which is then free from IC interference, is injected into a TOC instrument system. The organic carbon is oxidized to CO_2, which is released from the sample, detected, and reported as mg/L or ppm TOC or DOC.

2.5 The UVA procedure requires that the sample be passed through a 0.45-µm filter and transferred to a quartz cell. It is then placed in a spectrophotometer to measure the UV absorbance at 254 nm and reported in cm^{-1}.

2.6 The SUVA calculation requires both the DOC and UVA measurement. The SUVA is calculated by dividing the UV absorbance of the sample (in cm^{-1}) by the DOC of the sample (in mg/L) and then multiplying by 100 cm/M. SUVA is reported in units of L/mg-M. The formula for the SUVA may be found in Section 12.2.

3.0 DEFINITIONS AND TERMS

NOTE: *To assist the reader, a table of acronyms can be found in Section 3.20.*

3.1 ANALYSIS BATCH - A set of samples prepared and analyzed on the same instrument during a 24-hour period. For a TOC/DOC analysis batch, the set may contain: calibration standards, laboratory reagent blank and/or filter blanks, field blank, field samples, laboratory fortified matrix sample, field duplicate sample, and continuing calibration check standards. For a UVA analysis batch, the set may contain: filter blanks, field samples, field blank, field duplicate sample, and spectrophotometer check solutions with associated blank. An analysis batch is limited to 20 field samples. QC samples are not counted towards the 20 sample limit. QC requirements are summarized in Table 17.6.

3.2 BLANKS - Prepared from a volume of LRW (Sect. 3.9) and used as needed to fulfill quality assurance requirements and to monitor the analytical system.

3.2.1 CALIBRATION BLANK (CB) - The calibration blank is a volume of LRW that is treated with the same reagents used in the preparation of the calibration standards. The CB is a “zero standard” and is used to calibrate the TOC instrument. The CB is made at the same time as the calibration standards and stored along with and under the same conditions as the calibration standards. The CB is also used to monitor increases in organic background found in the

calibration standards over time by analyzing it as a sample and comparing the results with initial analysis of the CB.

3.2.2 FIELD REAGENT BLANK (FRB) - A volume, equivalent to that which is collected at a sample site, of LRW is placed in a sample bottle or vial. A second empty sample bottle or vial accompanies the LRW sample container to the sample site. At the sample site, the LRW is transferred into the empty bottle or vial which then becomes the FRB. The FRB is treated as a sample in all respects including shipment from the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if the TOC, DOC, and UVA measurements of the samples collected in the field are free from interferences or contamination as a result of the sample collection procedure and/or transport of the sample(s) to the laboratory. The FRB is optional and is usually used when the laboratory suspects a problem in sample collection and handling.

3.2.3 FILTER BLANK (FB) - The FB is an aliquot of LRW that is filtered and analyzed using the same procedures as field samples undergoing DOC and UVA determinations. For DOC and UVA analyses, the FB serves as the LRB. The FB will give an indication of overall contribution of organic carbon contamination from laboratory sources such as the LRW itself, labware cleaning procedures, reagents, the filter apparatus, filter, and instrument system(s).

3.2.4 LABORATORY REAGENT BLANK (LRB) - A volume of LRW that is prepared with each sample set and is treated exactly as a TOC sample including exposure to all glassware, plasticware, equipment, and reagents that are used with other samples. The LRB is used to determine if organic contamination or other interferences are present in the laboratory environment, reagents, apparatus, or procedures. The LRB must be acidified and sparged following the same procedure as is used to prepare the TOC sample(s).

3.3 CALIBRATION SOLUTIONS - Calibration should be performed according to the manufacturer's operation manual. The following solutions are used to calibrate the TOC instrument system for TOC or DOC determinations (calibration solutions are not used for UVA determination):

3.3.1 ORGANIC CARBON PRIMARY DILUTION STANDARD (OC-PDS) - A concentrated solution containing potassium hydrogen phthalate (KHP) in LRW water that is prepared in the laboratory or is an assayed KHP standard solution purchased from a commercial source. The OC-PDS is used for the preparation of organic carbon calibration standards (OC-CAL), continuing

calibration check standards (CCC), and laboratory fortified matrix samples (LFM).

3.3.2 ORGANIC CARBON CALIBRATION STANDARD (OC-CAL) - A solution prepared from the OC-PDS and diluted with LRW to various concentrations. The OC-CAL solutions are used to calibrate the instrument response with respect to organic carbon concentration.

3.3.3 CONTINUING CALIBRATION CHECK (CCC) - An OC-CAL solution which is analyzed periodically to verify the accuracy of the existing calibration of the instrument (Sect. 10.3).

3.4 DISSOLVED ORGANIC CARBON (DOC) - Organic matter, contained in a water sample that is soluble and/or colloidal, that can pass through a 0.45-µm filter.

3.5 FIELD DUPLICATES (FD1 and FD2) - Two separate samples collected at the same time and place under identical circumstances, and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as laboratory procedures.

3.6 INORGANIC CARBON (IC) - Carbon in water samples from non organic sources, composed mainly from dissolved mineral carbonates and carbon dioxide. IC can interfere with the determination of TOC and DOC if it is not removed.

3.7 LABORATORY FORTIFIED BLANK (LFB) – An aliquot of LRW or other blank matrix to which a known quantity of KHP is added in the laboratory. The LFB is subjected to the same preparation and analysis as a sample. The purpose of the LFB is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. For this method, a TOC LFB is the same as a CCC (Sect. 10.3) and no additional LFB is required. One LFB is required with each DOC analysis batch. No LFB is required for UVA analysis.

3.8 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) - An aliquot of a field sample to which a known quantity of KHP is added in the laboratory. The LFM is subjected to the same preparation and analysis as a sample, and its purpose is to determine whether the sample matrix affects the accuracy of the TOC or DOC analytical results. The background concentration of organic carbon in the sample matrix must be determined in a separate aliquot and the measured value in the LFM corrected for background concentration.

3.9 LABORATORY REAGENT WATER (LRW) - The LRW may be distilled and/or deionized (DI) water, or high pressure liquid chromatography (HPLC) reagent grade

or equivalent water which is low in TOC concentration, meeting the requirements as stated in Section 7.2.

3.10 MATERIAL SAFETY DATA SHEET (MSDS) - Written information provided by a vendor describing a chemical's toxicity, health hazards, physical and chemical properties (flammability, reactivity, etc.), storage, handling, and spill precautions.

3.11 MINIMUM REPORTING LEVEL (MRL) - The minimum concentration of organic carbon that can be reported as a quantified value in a sample following analysis. This concentration is determined by the background level of the analyte in the LRBs and the sensitivity of the method to organic carbon. See Section 9.10 for guidelines in the establishment of the MRL.

3.12 ORGANIC CARBON DETECTION LIMIT (OCDL) - The calculated minimum concentration of a known amount of organic carbon (OC) added to the LRW that can be identified, measured as either TOC or DOC, and reported with 99% confidence that the OC concentration is greater than zero as per the procedure in Section 9.2.7.

3.13 ORGANIC CARBON (OC) - In this method, when a concentration or instrument reading applies to either a TOC or DOC determination, the term "OC" may be used. For example, the LRB must not exceed 0.35 mg/L OC.

3.14 ORGANIC MATTER - A mixture of organic compounds (carbon-carbon, carbon-hydrogen bonded compounds) naturally occurring and/or man-made that are found in source water used by drinking water utilities. The quantity and quality of the OM in source water is measured by TOC/DOC instrument systems or is measured by UVA.

3.15 QUALITY CONTROL SAMPLE (QCS) - A solution containing a known concentration of an organic carbon compound(s) which is analyzed exactly like a sample. The QCS is obtained from a source external to the laboratory and is different from the source used for preparing the calibration standards. It is used to check laboratory and instrument performance.

3.16 SOURCE WATER - Surface water or ground water that is used by a drinking water utility to produce potable water for public consumption.

3.17 SPECIFIC UV ABSORBANCE AT 254 nm (SUVA) - A measure of DOC aromatic content that is calculated by measuring the DOC and the UV absorbance at 254 nm of a 0.45-µm filtered water sample. SUVA is calculated according to the equation given in Section 12.2.

3.18 TOTAL CARBON (TC) - A measure of the OC and IC contained in a water sample. In this method, IC is removed from the sample. Therefore, the TC reported by a TOC instrument system will be equal to the TOC or DOC measurement.

3.19 TOTAL ORGANIC CARBON (TOC) - The gross amount of organic matter (carbon not removed by the IC removal step) found in natural water. Suspended particulate, colloidal, and dissolved organic matter are a part of the TOC measurement. For this method, the TOC definition excludes the contribution of floating vegetative or animal matter, and volatile organic matter found in source water. Settleable solids consisting of inorganic sediments and some organic particulate are not transferred from the sample by the laboratory analyst and are not a part of the TOC measurement.

3.20 TABLE OF ACRONYMS

Acronym	Term
CB	calibration blank
CCC	continuing calibration check
COMM-BKS	commercial spectrophotometer background solution
COMM-SCS	commercial spectrophotometer check solution
DOC	dissolved organic carbon
FB	filter blank
FD	field duplicate
FRB	field reagent blank
IC	inorganic carbon
IDC	initial demonstration of capability
KHP	potassium hydrogen phthalate
LFB	laboratory fortified blank
LFM	laboratory fortified matrix
LRB	laboratory reagent blank
LRW	laboratory reagent water
MRL	minimum reporting level
MSDS	material safety data sheet
OC-CAL	organic carbon calibration standard

Acronym	Term
OC-PDS	organic carbon primary dilution standard
OCDL	organic carbon detection limit
QCS	quality control sample
SCS	spectrophotometer check solution
SDWA	Safe Drinking Water Act
SOP	standard operating procedure
SUVA	specific UV absorbance
TC	total carbon
TOC	total organic carbon
UVA	UV absorbance

4.0 CONTAMINATION AND INTERFERENCES

4.1 SPECIAL CONSIDERATIONS FOR ONSITE UTILITY LABORATORIES - Aerosols (foam and mist) from the operation of a water treatment plant contain organic carbon and will contaminate glassware, reagents, sample collection equipment, and onsite laboratory equipment if they are exposed to air at the water utility. For an onsite laboratory, it is recommended that air be filtered and isolated from organic fumes generated by petroleum products and combustion gases which come from the operation of some water utility equipment. Work traffic in the onsite laboratory should be minimized as it may produce dust containing organic matter that will result in the contamination of unprotected samples and laboratory equipment.

4.2 All glassware must be meticulously cleaned. Wash glassware with detergent and tap water, rinse with tap water followed by reagent water. Non-volumetric glassware may then be heated in a muffle furnace at 425 °C for 2 hours to eliminate interferences. Volumetric glassware should not be heated above 120 °C. Alternate cleaning procedures, such as acid rinsing and heating at lower temperatures, may be employed, providing that these procedures are documented in a laboratory SOP and LRBs are monitored as per Section 9.9.

4.3 Laboratory water systems have been known to contaminate samples due to bacterial breakthrough from resin beds, activated carbon, and filters. Laboratory water systems should be maintained and monitored frequently for carbon background and bacterial growth. It is recommended that the LRW be filtered through a 0.22-µm filter membrane to prevent bacterial contamination of TOC instrument systems, reagents,

and samples. The LRW, sample transfer (pipet), glassware, and sample bottles are the principle source for organic background in the analytical system. However, it is not possible to control all sources of organic carbon contamination. Therefore, this method allows for instrument background correction or adjusting the zero reference point of the instrument for organic carbon background that is found in the analytical system. [2] There are many ways to correct for organic carbon background. Consult the instrument manufacturer's operation manual for the instrument background correction procedure. **Subtraction of LRB or FB measurements from TOC, DOC, or UVA sample results is not allowed.**

4.4 High concentrations of OC, both man-made and naturally occurring, can cause gross contamination of the instrument system, changes in calibration, and damage to valves, pumps, tubing, and other components. It is recommended that analysis of a sample known to have a concentration of OC > 10 mg/L OC be followed by the analysis of an LRB. It is highly recommended that known samples containing OC concentrations > 50 mg/L OC be diluted or not run on instruments used to analyze low-level drinking water samples.

4.5 Source waters containing ionic iron, nitrates, nitrites, and bromide have been reported to interfere with measurements of UVA absorbance at 254 nm. [3] The concentration of the interferences and their effect on the UVA cannot be determined as each unique sample matrix may produce a different UVA response for the same concentration of interference or combination of interferences. This method does not treat or remove these interferences. Therefore, suspected or known interferences may affect results and must be flagged in the SUVA result as "suspected UVA interferences."

4.6 Chloride exceeding 250 mg/L may interfere with persulfate oxidation methods.[4, 5] Some instrument systems may require increased persulfate concentration and extended oxidation times. Consult with your instrument manufacturer's representative or instrument operation manual for instrument settings and reagent strengths when analyzing samples containing high levels of chloride.

4.7 Inorganic carbon (IC) interferes with TOC and DOC measurements. TOC instrument bias due to incomplete IC removal has been reported.[6, 7] If inorganic carbon is not completely removed from the water sample, it will result in a positive or negative bias depending on the way the instrument system calculates TOC (e.g., TOC =TC - IC, TC = TOC + IC, or TOC = TC). When inorganic carbon (IC) is removed from the sample prior to the TOC assay, as required in this method, TOC = TC and the method bias is minimized.

5.0 SAFETY

5.1 Fast-moving source water, steep inclines, water conduits, and electrical hazards may present special safety considerations for the sample collector. The sample collector

should be aware of any potential safety hazards and take necessary precautions while collecting samples.

5.2 Each chemical reagent used in this method should be regarded as a potential health hazard. Exposure to these compounds should be minimized and/or avoided by active participation in safety planning and good laboratory practices.[8] Each laboratory is responsible for maintaining a current awareness file of OSHA regulations[9] regarding the safe handling of the chemicals specified in this method. Material Safety Data Sheets (MSDS) containing information on chemical and physical hazards associated with each chemical should be made available to all personnel involved in the chemical analysis.

5.3 Potassium persulfate is a strong oxidizing and corrosive reagent. The analyst should avoid eye and skin contact by wearing eye/face protection, powderless gloves and laboratory clothing. If body tissue comes in contact with this reagent, apply large quantities of water for at least 15 minutes (see MSDS) while removing contaminated clothing. This reagent may cause delayed burns. Seek immediate medical attention if the area becomes irritated or burned. This reagent can also cause a fire or explosion if it is allowed to come in contact with combustible materials.

5.4 Protect your hands by wearing laboratory disposable gloves during the preparation and disposal of corrosive (acids and oxidants) laboratory reagents. Do not reuse laboratory gloves that have been discarded or are suspected of being contaminated.

6.0 EQUIPMENT AND SUPPLIES

NOTE: *Brand names, and/or catalog numbers are included for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus, instrument systems, and reagents other than those that are illustrated below. The laboratory is responsible for the assurance that alternate products, apparatus, instrument systems, and reagents demonstrate equivalent performance as specified in this method.*

6.1 FILTER APPARATUS - Nalgene® or Corning® 250 mL Filter System, 0.45-µm Nylon (NYL) or Polyethersulfone (PES) Low Extractable Membrane/Polystyrene Body with optional glass fiber prefilters (nominal 1 to 7 um). Packaging and filter apparatus are recyclable (NALGE-NUNC International: Nalgene Labware CAT. numbers NYL: 153-0045, PES: 168-0045). It is recommended that filter membranes be hydrophilic 0.45-µm filter material.

NOTE: *Alternate filter membranes (e.g., polypropylene, silver or Teflon®), apparatus technologies such as cartridges, reusable filter bodies, syringe filters, and their associated syringes, peristaltic pumps or vacuum pumps may be selected. The complexity of an alternative filter apparatus is left to the analyst's ingenuity providing that the apparatus meets quality control and initial demonstration of*

capability requirements as stated in Section 9.3.2, and that FB requirements are met (Sect. 9.9). It is recommended that the analyst review the AWWA journal article "Selecting filter membranes for measuring DOC and UV_{254}", Karanfil, et. al.[10], prior to the selection of an alternative filter membrane, apparatus, and wash procedure. Karanfil tested 11 filter membranes (0.45-µm pore size and 47-mm disc size) representing four different manufacturers and seven different types of filter materials for both desorption and adsorption. Hydrophilic polyethersulfone (PES) filters available from two manufacturers (Osmonics Micro-PES and Gelman Supor 450, both 0.45 micron absolute pore size and 47-mm disc size) and a hydrophilic polypropylene filter (Gelman GH Polypro, 0.45 micron absolute pore size and 47-mm disc size) were found to be the best options among those tested in the study.

6.2 INJECTION VIALS - Specially cleaned 40-mL glass vials, with caps and polytetrafluoroethylene (PTFE)/silicone septa. Eagle-Picher TOC Certified, Cat. No. 40C-TOC/LL, Eagle-Picher Technologies®. These vials are specially cleaned by the manufacturing process and certified to contain < 10 µg TOC. Vials may be reused if cleaned as per Section 4.2. The PTFE/silicone septa once pierced by the sample injector must be discarded.

6.3 INSTRUMENT SYSTEMS - The TOC and UVA procedures allow for the use of several different types or combinations of TOC instrumental system technologies. Examples of typical TOC instrument systems, as well as a UV spectrophotometer, are described below. Data from these instruments may be found in Section 17. Only one TOC instrument is required to perform this method.

6.3.1 TOC INSTRUMENT 1: UV/Persulfate/Wet Oxidation with Permeation/Conductivity Detection. The Ionics-Sievers® 800 TOC analyzer is based on UV catalyzed persulfate digestion to produce CO_2, which is detected by a membrane permeation/conductivity detector.

6.3.2 TOC INSTRUMENT 2: Elevated Temperature/Catalyzed/Persulfate/Wet Oxidation/Nondispersive Infrared Detection (NDIR). The O.I. Analytical® TOC Model 1010 is based on elevated temperature (95-100°C) catalyzed persulfate digestion to produce CO_2, which is then detected by an NDIR detector.

6.3.3 TOC INSTRUMENT 3: UV/Low Temperature/Persulfate/Wet Oxidation/NDIR. The Tekmar-Dohrmann® Phoenix 8000 TOC analyzer is based on UV catalyzed persulfate digestion to produce CO_2, which is then detected by an NDIR detector.

6.3.4 TOC INSTRUMENT 4: Catalyzed/Combustion Oxidation(680 °C)/NDIR. The Shimadzu® model TOC-5000A analyzer is based on a catalyzed

combustion in air or oxygen reagent gas to produce CO_2, which is then detected by an NDIR detector.

6.3.5 TOC INSTRUMENT 5: High Temperature Combustion Oxidation/NDIR. The Thermo Environmental® ThermoGlas™ 1200 TOC is based on a dual zone furnace with individually adjustable ovens from 700 to 1250 °C for final high temperature combustion of the sample with air or oxygen reagent gas to produce CO_2, which is then detected by an NDIR detector.

6.3.6 UV SPECTROPHOTOMETER: The spectrophotometer is used for the UVA determination only. The spectrophotometer must be able to measure UVA (254 nm), with an absorbance from 0.0045 to at least 1.0 cm^{-1} UVA, and accommodates a sample cell with a path length of 1, 5, or 10 cm.

6.4 LABORATORY REAGENT WATER TREATMENT SYSTEM - The LRW used for the development of this method was generated using a Millipore®, Milli-Q Plus Ultra-Pure Water Treatment System with a 0.22-µm sterile pack filter capable of producing organic carbon free (< 0.010 mg/L OC), ultrapure deionized water.[11] The maximum amount of OC allowed in the LRW for this method is 0.35 mg/L. When purchasing a treatment system for general laboratory use, it is recommended that a system be purchased capable of producing LRW of the above stated quality in order to be of use in other laboratory analyses.

6.5 MUFFLE FURNACE - A muffle furnace capable of heating up to 425 °C.

6.6 FIELD SAMPLE pH TEST - Sample pH indicator test strips, non-bleeding (colorpHast® Indicator Strips 0 - 2.5, cat. 9580), EM Science, 480 Democrat Road, Gibbstown, N.J. 08027. Pocket pH test kits, pocket pH meters, or laboratory pH meters are acceptable for field sample pH measurements.

6.7 PIPET, DISPOSABLE TRANSFER - Large volume bulb (15mL), non-sterile, with flexible long stem polyethylene transfer pipet. "Sedi-Pet ™", Fisher Scientific® Cat. 13-711-36. Pipets are used for sample transfer from the middle of a sample bottle containing floating material (scum).

6.8 SAMPLE COLLECTION REAGENT BOTTLES - Specially cleaned, 1-L Boston round glass bottles with cap. Eagle-Picher TOC Certified, Cat. No. 112-01A/C TOC, Eagle-Picher Technologies, LLC. These bottles are specially cleaned by the manufacturing process and certified to meet EPA OSWER Directive # 9240.0-05A "Specifications And Guidance For Contaminant-Free Sample Containers 12/92." Amber bottles are preferred, but clear glass bottles may be used if care is taken to protect samples from light. The laboratory may select glass bottles of any volume that meet the utility and laboratory sample processing and quality control sampling needs.

Glass bottles may be reused after cleaning (see Sect. 4.2 for glassware cleaning instructions) or discarded.

6.9 SPARGE APPARATUS - N-EVAP™, Nitrogen Evaporator System Model 111, Organomation Associates Inc. This apparatus is not used for its originally designed purpose of evaporating sample extracts. In this method, the apparatus is used as a sparging device. The stainless steel needles of the apparatus are lowered into the 40-mL sample vials containing the TOC or DOC samples to remove inorganic carbon by sparging with nitrogen gas.

Alternately, some TOC auto-samplers provide a pre-sparging or membrane IC removal option prior to injection of the sample into the TOC instrument system. The analyst is encouraged to utilize these instrument options, if available. Another alternative is for the laboratory analyst to fabricate a sparging apparatus. For example, an apparatus may consist of copper tubing from a regulated gas source, connected to a needle valve used for gas flow control, a length of silicone tubing with a glass Pasteur pipet inserted into the tubing and a ring stand with clamp for positioning the pipet. The Pasteur pipet is inserted into the sample bottle or vial to remove inorganic carbon by sparging with nitrogen gas (Sect. 11.5). The complexity of the alternative sparging apparatus is left to the analyst's ingenuity providing that the apparatus meets quality control and initial demonstration of capability (IC removal test) requirements as stated in Section 9.2.4.

6.10 VACUUM SOURCE - Aspirator, air flow or water flow, hand-operated or low pressure electric vacuum pump, providing a vacuum of 15 inches of mercury (Hg) or better. If an alternative choice is made, see note in Section 6.1.

6.11 VARIABLE PIPETTES - Programable automated pipettes. Rainin Instrument® EDP-Plus Pipette 10ml, Cat. No. EP-10 mL; EDP-Plus Pipette 1000 µL, Cat. No. EP-1000; EDP-Plus Pipette 100 µL, Cat. No. EP-100, or manual variable pipets with disposable tips having a calibrated range of 0 to 100-µL, 0 to 1000-µL, and 0 to 10 mL.

6.12 VOLUMETRIC FLASK AND PIPETS - All volumetric glassware used in this method are required to be "Class A".

6.13 WAVELENGTH VERIFICATION FILTER SET- Wavelength verification may be provided by the instrument manufacturer, a scientific instrument service company, or if this not practical, wavelength verification may be made by the laboratory using certified spectrophotometric filter sets with values traceable to NIST. Fisher Scientific Cat. No. 14-385-335, Spectronic No. 333150.

7.0 REAGENTS AND STANDARDS

NOTE: *The chemicals required for this method must be at least reagent grade. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS) and/or ACS certified, when available. Some instrument manufacturers provide reagents specifically prepared for the optimum performance of their TOC instruments and provide calibration services and/or calibration standards. The analyst is allowed to use these services or prepare reagents and/or standards according to the instrument manufacturer's operation manual.*

7.1 COMPRESSED GASES – Carbon dioxide free Ultra High Purity (UHP) grade nitrogen gas or an optional Ultra-low level TOC gas delivery system. For combustion based TOC systems, zero grade air and UHP grade oxygen may be needed. The use of lesser grades of compressed gases will result in high background noise in the TOC instrument systems. The TOC Instrument 1 described in Section 6.3.1. does not require compressed gasses for operation.

7.2 LABORATORY REAGENT WATER (LRW) - Water that has a TOC reading of $\leq$ 0.35 mg/L and $\leq$ 0.01 cm^{-1} UVA. Although the LRW TOC and UVA limits in this method are 0.35 mg/L and 0.01 $cm^{-1,}$ respectively, the system specified in Section 6.4 is capable of producing better quality organic carbon free, ultrapure deionized water. For optimum performance, it is recommended that LRW with $\leq$ 0.05 mg/L TOC and $\leq$ 0.0045 cm^{-1} UVA be used for this method. Alternatively, LRW may be purchased (ACS HPLC grade or equivalent).

7.3 DISODIUM HYDROGEN PHOSPHATE, [Na_2HPO_4, CAS# 7558-79-4] - Anhydrous, ACS grade or better.

7.4 O-PHOSPHORIC ACID (85%), [H_3PO_4, CAS# 7664-38-2] - ACS grade or better.

7.5 POTASSIUM DIHYDROGEN PHOSPHATE, [KH_2PO_4, CAS# 7778-77-0]- Anhydrous, ACS grade or better.

7.6 POTASSIUM HYDROGEN PHTHALATE (KHP), [$C_8H_5O_4K$, CAS# 877-24-7] - Anhydrous, ACS grade or better.

7.7 REAGENT SOLUTIONS FOR WET CHEMICAL OXIDATION - It is assumed that each instrument manufacturer has optimized reagent solutions for their respective instruments and has provided the instructions for the preparation of reagents in the instrument's operation manual. NOTE: *TOC Instrument 1 does not require gas sparge of reagents as the manufacture provides reagent packs for the operation of the instrument.*

7.7.1 PERSULFATE REAGENT - Prepare this solution according to the instrument manufacturer's instructions or purchase the solution from the instrument manufacturer. If the laboratory prepares the solution, transfer the solution to the instrument reagent bottle and cap. It is recommended that this solution be sparged gently with carbon dioxide free UHP grade nitrogen gas for approximately 1 hour. If the instrument system provides continuous sparge, it is recommended that the reagent bottles be allowed to sparge for 10 minutes to 1 hour before operating the instrument. Self contained reagent packs or other types of reagent systems may not require reagent sparging. Discard the solution as per expiration time/date listed in the manufacturer's operation manual.

7.7.2 PHOSPHORIC ACID SOLUTION - Prepare this solution according to the instrument manufacturer's instructions or purchase the solution from the instrument manufacturer. If the laboratory prepares the solution, transfer the solution to the instrument reagent bottle and cap. It is recommended that this solution be sparged gently with carbon dioxide free UHP grade nitrogen gas for approximately 1 hour. If the instrument system provides continuous sparge, it is recommended that the reagent bottles be allowed to sparge for 10 minutes to 1 hour before operating the instrument. Self contained reagent packs or other types of reagent systems may not require reagent sparging. Discard the solution as per expiration time/date listed in the manufacturer's operation manual.

7.8 STANDARD SOLUTIONS

NOTE: *Consult with the instrument manufacturer or operation manual for the recommended concentrated acid used for preservation of standard solutions. The concentrated acid used to preserve the standards is usually HCl, H_2SO_4, or H_3PO_4 depending upon the instrument operation manual recommendation. The acid used for the standards must be the same as the one used for the samples. Standard solutions may be alternatively prepared in larger or smaller volumes and concentrations as needed for the calibration of instruments. Standard solutions may be prepared by gravimetric or volumetric techniques. This section provides guidance for the preparation of calibration solutions.*

7.8.1 INORGANIC CARBON PRIMARY TEST SOLUTION (IC-TEST) REAGENTS

7.8.1.1 AMMONIUM CHLORIDE, [NH_4Cl, CAS# 12125-02-9] - ACS grade or better.

7.8.1.2 CALCIUM CHLORIDE DIHYDRATE, [$CaCl_2 \cdot 2H_2O$, CAS# 10035-04-8] - ACS grade or better.

7.8.1.3 CALCIUM NITRATE TETRAHYDRATE, [$Ca(NO_3)_2 \cdot 4H_2O$, CAS# 13477-34-4] - ACS grade or better.

7.8.1.4 MAGNESIUM SULFATE HEPTAHYDRATE, [$MgSO_4 \cdot 7H_2O$, CAS# 10034-99-8] - ACS grade or better.

7.8.1.5 POTASSIUM CHLORIDE, [KCl, CAS# 7447-40-7] - ACS grade or better.

7.8.1.6 SODIUM BICARBONATE, [$NaHCO_3$, CAS# 144-55-8] - ACS grade or better.

7.8.1.7 SODIUM CHLORIDE, [NaCl, CAS# 7647-14-5] - ACS grade or better.

7.8.1.8 SODIUM-META SILICATE NONAHYDRATE, [$Na_2SiO_3 \cdot 9H_2O$, CAS# 13517-24-3]

7.8.1.9 SODIUM PHOSPHATE DIBASIC HEPTAHYDRATE, [$Na_2HPO_4 \cdot 7H_2O$, CAS# 7782-85-6] - ACS grade or better.

7.8.2 PREPARATION OF THE IC-TEST SOLUTION, 100 MG/L IC - This solution is used in the performance of the IC removal sparging efficiency test (Sect. 9.2.4). The ionic content of the IC-TEST mixture solution was chosen from a previous investigation in which the authors wanted to simulate waters likely to be found in waste treatment plants.[12] Because the inorganic salts are not soluble in a single concentrated solution, prepare four separate stock solutions by diluting each of the following to one liter with LRW:

FLASK (1 L)	SALT	WEIGHT (g)
A	magnesium sulfate heptahydrate, $MgSO_4 \cdot 7H_2O$	2.565
B	ammonium chloride, NH_4Cl	0.594
	calcium chloride dihydrate, $CaCl_2 \cdot 2H_2O$	2.050
	calcium nitrate tetrahydrate, $Ca(NO_3)_2 \cdot 4H_2O$	0.248
	potassium chloride, KCl	0.283
	sodium chloride, NaCl	0.281
C	sodium bicarbonate, $NaHCO_3$	2.806
	sodium phosphate dibasic heptahydrate, $Na_2HPO_4 \cdot 7H_2O$	0.705
D	sodium-meta silicate nonahydrate, $Na_2SiO_3 \cdot 9H_2O$	1.862

Prepare a 102.5 mg/L IC-TEST mixture, based on bicarbonate calculations and impurities, by adding a 10-mL aliquot of each of the above solutions to a 40-mL vial. Add 40 µL of H_3PO_4, HCl, or H_2SO_4, depending upon instrument requirements (see note, Sect. 7.8), to the 40-mL injection vial. An IC-TEST mixture of approximately 100 mg/L was chosen to represent the extreme inorganic carbon concentration the analyst may encounter. Although the mixture is turbid after preparation, clarification occurs after acidification.

7.8.3 ORGANIC CARBON PRIMARY DILUTION STANDARD (OC-PDS), 500 mg/L (1 mL = 0.5 mg OC) - Prepare an acid preserved (pH $\leq$2) OC-PDS by pouring approximately 500 mL of LRW into a 1-liter volumetric flask, adding 1 mL of concentrated acid for preservation (see note, Sect. 7.8), carefully transferring 1.063 g KHP into the LRW, stirring until it is dissolved, and then diluting to the mark with LRW (1.0 mg KHP = 0.471 mg Organic Carbon). Transfer this solution to a marked amber glass reagent bottle and cap for storage. This solution does not require refrigeration for storage and is stable for an indefinite period of time (6 months to a year). Replace the OC-PDS if the instrument system fails to pass the QCS requirements (Sect. 9.11).

7.8.4 ORGANIC CARBON CALIBRATION (OC-CAL) - At least 4 calibration concentrations and the CB (i.e., a minimum of 5 total calibration points) are required to prepare the initial calibration curve. Prepare the calibration standards over the concentration range of interest from dilutions of the OC-PDS. The calibration standards for the development of this method were prepared as specified in the table below. Calibration standards must be

prepared using LRW preserved to pH ≤ 2 with concentrated acid (see note, Sect. 7.8). Filtration of the CAL standards for DOC analysis is unnecessary, since interferences from the filtration unit are monitored via the FB. Therefore, the OC-CAL may be applied to TOC or DOC determinations. The OC-CAL standards must be sparged, or otherwise treated for IC removal, like a sample following the procedure in Section 11.5.

PREPARATION OF CALIBRATION (OC-CAL) CURVE STANDARDS				
CAL Level	Initial Conc. of OC-PDS (mg/L)	Vol. of OC-PDS (mL)	Final Vol. of OC-CAL Std. (mL)	Final Conc. of OC- CAL Std. (mg/L)
CB	–	0	1000	–
1	500	1.0	1000	0.5
2	500	2.0	1000	1.0
3	500	4.0	1000	2.0
4	500	10.0	1000	5.0
5	500	20.0	1000	10.0
6 *	500	5.0	100	25.0
7 *	500	10.0	100	50.0

* Note: OC-CAL 6 - 7 are optional calibration standards for use when operating the instrument in a higher concentration range.

The calibration blank (CB) is a "0.0 mg/L OC " standard which approximates zero mg/L OC concentration plus the background carbon contributed from the LRW. The CB is stored and treated the same as all other calibration standards. When analyzed, the CB must not exceed 0.35 mg/L TOC.

7.8.5 Calibration standards may be stored at room temperature in amber glass bottles (Sect. 6.8) and/or in a dark cabinet (if clear glass used) for a period of 30 days. If stored OC-CALs are used to recalibrate the instrument during this 30 day period, the CB which has been stored with the OC-CALs must be analyzed as a sample prior to recalibration. The CB must not exceed 0.35 mg/L OC. If the CB does not meet this criteria, the CB and OC-CALs may have absorbed OC from the laboratory atmosphere and must be discarded.

7.9 COMMERCIAL SPECTROPHOTOMETER CHECK SOLUTION (COMM-SCS) - The laboratory may use a commercially prepared COMM-SCS for the purpose of checking the performance of the spectrophotometer. The analyst should purchase the COMM-SCS in the absorbance range that is commonly observed for the samples

analyzed. The IN-SPEC™ optical standard and background solution for a 254 nm spectrophotometric check is NIST traceable, and is available from GFS Chemicals, PO Box 245, Powell, Ohio 43065.

7.9.1 COMMERCIAL SPECTROPHOTOMETER BACKGROUND SOLUTION (COMM-BKS) - A background solution provided by the COMM-SCS provider that is used to correct for stabilizing agents present in the COMM-SCS.

7.10 LABORATORY PREPARED KHP-SPECTROPHOTOMETER CHECK SOLUTIONS (KHP-SCS) - The laboratory may elect to prepare a KHP based spectrophotometer check solution (KHP-SCS) for the purpose of checking the performance of the spectrophotometer at the absorbance of the average UVA sample. This requires the preparation of a buffered KHP solution having a known concentration and a known absorbance at 254 nm. The analyst should prepare the KHP-SCS that will provide an absorbance similar to the absorbance in the range (low, mid, high) of the sample analyzed. NOTE: *If the phosphate buffer reagents used below have been exposed to laboratory humidity, it is recommended that potassium dihydrogen phosphate (KH_2PO_4) and disodium hydrogen phosphate (Na_2HPO_4) be dried for 1 hour at 105°C.*

7.10.1 KHP-SCS-BLANK - Prepare a 1-L volumetric flask containing approximately 500 mL of LRW. Transfer and dissolve 4.08 g anhydrous KH_2PO_4 and 2.84 g anhydrous Na_2HPO_4 in 500 mL. Dilute to the mark with LRW and transfer to a 1-L amber glass bottle.

7.10.2 KHP-SCS - Prepare the KHP-SCS that will provide an absorbance similar to the absorbance of the samples analyzed. Prepare a 1-L volumetric flask containing approximately 500 mL of LRW. Transfer and dissolve 4.08 g anhydrous KH_2PO_4 and 2.84 g anhydrous $Na_2 HPO_4$ into the 500 mL of LRW. From the example calculation, or table located below (Sect. 7.10.2.1), transfer the amount of OC-PDS (in mL) needed to produce the representative absorbance of the sample into the buffered KHP-SCS and dilute with LRW to the 1 L mark.

7.10.2.1 KHP-SCS, CONCENTRATION CALCULATION - Standard Method 5910 B provides for a spectrophotometer check using a correlation equation which was based on the analyses of 40-samples of KHP solution. [3] The correlation formula is as follows: UV_{254} = 0.0144 KHP + 0.0018. This formula may be algebraically solved for the concentration of KHP, expressed as mg/L OC, needed to produce a KHP-SCS for the observed sample absorbance as follows:

$$\text{KHP-OC conc.} = (UV_{254} - 0.0018) \div 0.0144$$

Using the calculated KHP-OC concentration, determine the amount of OC-PDS (Sect. 7.8.3, 1 mL = 0.5 mg OC) needed to produce a known absorbance for the KHP-SCS. For example, if you typically run samples that have an average UVA equal to 0.08 cm^{-1}, you can calculate the KHP in the following manner:

$$5.431 \text{ KHP mg/L as OC} = (0.08\ cm^{-1}\ UVA_{254} - 0.0018) \div 0.0144$$

The 5.431 mg/L is the same as 5.431 mg/L KHP. It follows that to produce a 1-L KHP-SCS solution having a UVA absorbance of 0.08 cm^{-1}, you will need 10.9 mL of OC-PDS as calculated below:

(5.431 KHP-SCS mg/L)(1000mL/L) / 500 OC-PDS mg/L = 10.9 mL of OC-PDS

In summary, 10.9 mL OC-PDS is needed to make a 1-L KHP-SCS solution that will have a UVA absorbance of 0.08 cm^{-1}.

Alternately, the following table, which is based on the above calculation, can be used. From this table, cross reference the amount of the OC- PDS (in mLs) needed to produce the desired UVA for the KHP-SCS. Transfer the required amount of OC-PDS into a 1-L flask and dilute to the mark with LRW.

KHP-SCS Preparation		
UVA@254nm (cm^{-1})	**ORGANIC CARBON (mg/L)**	**OC-PDS (mL added per liter of LRW)**
0.0738	5	10
0.1458	10	20
0.2898	20	40
0.4338	30	60

7.10.3 Verify that the KHP-SCS-BLANK and the KHP-SCS buffered solutions are at pH 7. Check the pH by placing a drop from the SCS bottle onto pH test paper. **Do not put the pH paper into the SCS bottle.** Placing the pH paper in the bottle will contaminate the sample with organic carbon. If this happens, the spectrophotometer check solution must be discarded and a new solution prepared in a clean bottle. If the buffered KHP-SCSs are not at a pH of 7, the

solution must be discarded and a new solution made. Store these solutions at approximately ≤ 6 °C. These solutions are not preserved. In a sterile environment these solutions may be stable for a month. However, the shelf life of these solutions may be shortened as a result of microbial growth. Therefore, it is recommended that the above solutions be made fresh weekly and/or be replaced if any significant change in absorbance is noted.

8.0 SAMPLE COLLECTION, FILTRATION, AND HOLDING TIMES

NOTE: *Consult with the instrument manufacturer or operation manual for the recommended type of concentrated acid used for preservation of TOC or DOC samples. The concentrated acid used to preserve the sample is usually HCl, H_2SO_4, or H_3PO_4 depending upon the instrument operation manual recommendation. The acid used for the standards must be the same as the one used for the samples. Samples for DOC and UVA analyses may be filtered in the field using alternate apparatus technologies such as cartridges, reusable filter bodies, syringe filters, and their associated syringes, peristaltic pumps or vacuum pumps providing that the filter blank requirements are met (Sect. 9.9).*

8.1 SUVA SAMPLE COLLECTION - SUVA is determined by the analysis of a DOC sample and a UVA sample, together called the SUVA sample set. A single sample may be collected and split for the DOC and UVA analyses or two individual samples may be collected at the same time. For example: if the sample is to be determined by two separate laboratories (i.e., one lab determines UVA and a second lab determines the DOC), the sample collector may collect two representative samples for shipment. A 1-L volume is recommended for the collection of DOC and UVA samples, but other volumes may be collected depending on the sample volume needed for the filtration apparatus used by the analyzing laboratory. The SUVA sample set is collected in clean glass bottles by filling the bottle almost to the top. The sample set is **NOT preserved with acid** at the time of collection. The sample set is delivered as soon as possible to the laboratory and should arrive packed in ice or frozen gel packs. The sample set is processed by the laboratory and stored at ≤ 6 °C, until analysis. If there is no visible ice or the gel packs are completely thawed, the laboratory should report these conditions to the data user. Samples shipped that are improperly preserved, and/or do not arrive at the laboratory within 48 hrs, cannot be used to meet compliance monitoring requirements under the Safe Drinking Water Act (SDWA).

8.1.1 The DOC sample must be filtered in the field or in the laboratory within 48 hours of sample collection according to the procedure detailed in Section 11.4 prior to acidification and analysis. After filtration, the DOC sample is acidified with 1 mL of concentrated acid per 1 L of sample or the sample is preserved by drop wise adjustment to a pH ≤ 2 (Sect. 8.3). The DOC bottle is capped and inverted several times to mix the acid and is stored at ≤ 6 °C. The sample must be analyzed within 28 days from time of collection.

8.1.2 The UVA sample must be filtered in the field or in the laboratory according to the procedure detailed in Section 11.4. The sample used for the UVA determination is **not** acidified. The UVA bottle is capped and stored at ≤ 6 °C for up to 48 hours from the time of collection. The UVA sample must be analyzed within 48 hours from the time of collection.

8.2 TOC SAMPLE COLLECTION - The typical sample volume collected may vary from 40 mL to 1 L of sample. It is recommended that the sample collector coordinate the size of collection volume with the needs of the analytical laboratory. If the TOC sample is collected in a 40-mL injection vial, it is acidified to pH ≤ 2 by adding 2 drops of concentrated acid. If the TOC sample is collected in a 1-L bottle, 1 mL of concentrated acid is added or the sample is drop wise adjusted to a pH ≤ 2 (Sect. 8.3). TOC samples must be acidified at the time of collection. Cap the bottle or injection vial and invert several times to mix the acid. The sample is delivered as soon as possible to the laboratory and should arrive packed in ice or frozen gel packs. If there is no visible ice or the gel packs are completely thawed, the laboratory should report the conditions to the data user. Samples that are improperly preserved or shipped, cannot be used for compliance monitoring under the SDWA. The sample is stored at ≤ 6 °C, until analysis. Stored and preserved samples must be analyzed within 28 days from time of collection.

8.3 SAMPLE pH CHECK - The pH of the preserved sample (DOC, TOC only) or filtrate should be checked to ensure adequate acidification for the preservation. This should only be performed by an adequately trained sample collector. Check the pH by placing a drop from the sample onto pH test paper. **Do not** put the pH paper into the sample bottle. Placing the pH paper in the sample bottle will contaminate the sample with organic carbon. If this happens, the sample or filtrate must be discarded and a new sample collected.

9.0 QUALITY CONTROL

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. QC requirements for TOC include: the initial demonstration of laboratory capability (IDC) followed by regular analyses of continuing calibration checks (CCC), independent quality control samples (QCS), laboratory reagent blanks (LRB), field duplicates (FD), and laboratory fortified matrix samples (LFM). For this method, a TOC laboratory fortified blank (LFB) is the same as a CCC (Sect. 10.3) and no LFB is required. QC requirements for DOC include: the IDC followed by regular analyses of CCCs, QCSs, filter blanks (FB), LFB, FDs, and LFMs.

For laboratories analyzing both TOC and DOC samples, only the DOC IDC determination is required, as it is similar to, yet more rigorous than, the TOC IDC. The IDC must be performed the first time a new instrument is used and/or when a new analyst is trained.

QC requirements for UVA analysis include: the performance of the IDC followed by the regular analysis of spectrophotometer check solutions (SCS), FBs, and FDs. For UVA analysis, no LFB or DL determination is required.

The control of instrument background is crucial prior to the performance of the IDC. It is required that a critical evaluation be made of the instrument background [2] associated with an instrument system before proceeding with the IDC. Once an acceptable instrument background is established, it is safe to proceed with the IDC.

In summary, this section describes the minimum acceptable QC program, and laboratories are encouraged to institute additional QC practices to meet their specific needs. The laboratory must maintain records to document the quality of the data generated. All users of this method are encouraged to write their own SOPs stating exactly how their lab executes the method. A summary of QC requirements can be found in Tables 17.5 and 17.6.

9.2 INITIAL DEMONSTRATION OF CAPABILITY FOR TOC DETERMINATION

9.2.1 INITIAL DEMONSTRATION OF LOW SYSTEM BACKGROUND - Before any samples are analyzed, and any time a new set of reagents is used, prepare a laboratory reagent blank (LRB) and demonstrate that it meets the criteria in Section 9.9.

9.2.2 INITIAL INSTRUMENT CALIBRATION VERIFICATION - Prior to the analysis of the IDC samples, calibrate the TOC instrument as per Section 10.2. Verify calibration accuracy with the preparation and analysis of a QCS as defined in Section 9.11.

9.2.3 INITIAL ORGANIC CARBON FLOW INJECTION MEMORY CHECK - Inject the highest OC-CAL used, followed by two injections of the LRB. If the first LRB is > 0.35 mg/L OC and the second LRB is in QC compliance (i.e., $\leq$ 0.35 mg/L OC), a memory problem is indicated. Therefore, an LRB may need to be placed after every sample. If the instrument system provides a rinse or system flush with LRB between injections, activate the event control settings and repeat this section. If the memory problem persists, then an LRB must be placed after every sample.

9.2.4 INORGANIC CARBON REMOVAL SPARGING EFFICIENCY TEST- Various sample sparge times (3-10 minutes) and sparging flow rates have been reported for the removal of IC. [13] A multi-laboratory study reported large variations and positive bias in analyses of solutions of standards containing even small amounts of IC, demonstrating the importance of IC removal.[14] Since IC must be removed in order to reduce interferences with the TOC and

DOC quantitation, an IDC of the IC removal is performed. Please note: any manipulation of the sample may inadvertently introduce organic carbon from the apparatus.

Prepare an inorganic carbon mixture, IC-TEST solution, as specified in Section 7.8.2. Using the procedure outlined in Section 11.5, sparge at least three portions of the acidified IC-TEST solution in the same manner, and of the same volume, as field samples will be sparged. After the IC-TEST solution is treated by the IC removal apparatus, analyze the solution as an LRB for OC. The IC removal apparatus must produce an acceptable IC-TEST by meeting the LRB requirements as stated in Section 9.9. These IC removal parameters are then used for all subsequent samples.

The sparging time recommended in Section 11.5.2 is based on a sparging study with an N_2 flow rate of approximately 200 mL/min and a pH of 2.0. The following inorganic carbon concentration reduction was observed after the external sparging of a 40-mL IC-TEST solution:

IC REMOVAL SPARGE EFFICIENCY STUDY					
sparging time (minutes)	0	5	10	15	20
concentration IC (mg/L), measured as OC interference	102.5	6.11	0.611	0.049	0.044

The LRB during the above study was < 0.05 mg/L, thus a 20-minute sparge time ensured that no measurable organic carbon remained in the sample.

The above sparge efficiency table should be used only as a guide. The analyst may find that a higher flow rate may reduce the time necessary to remove the inorganic carbon to a level at or near the TOC measurements found in the LRB. The IC-TEST solution is also used to test alternate IC removal apparatus that remove IC by internal chemical treatment, alternate sparging procedures, and/or membrane IC removal. Any alternative procedure or IC removal apparatus must be tested using the IC-TEST solution and meet the LRB requirements as stated in Section 9.9.

9.2.5 INITIAL DEMONSTRATION OF ACCURACY - The initial demonstration of accuracy consists of the analysis of five (5) LFBs analyzed as samples at a concentration between 2 to 5 mg/L OC. If DOC analysis is being performed, the LFB must be filtered according to the procedure in Section 11.4. The average recovery between 2 to 5 mg/L OC must be within ±20% of the true

value. If ±20% of the true value is exceeded, identify and correct the problem and repeat Sections 9.2.5 and 9.2.6.

9.2.6 INITIAL DEMONSTRATION OF PRECISION - Calculate the average precision of the replicates in the Initial Demonstration of Accuracy (Sect. 9.2.5). The RSD% must be no greater than 20%. If the RSD% exceeds 20%, identify and correct the problem and repeat Sections 9.2.5 and 9.2.6.

9.2.7 ORGANIC CARBON DETECTION LIMIT (OCDL) DETERMINATION - The OCDL determination must be conducted over at least three (3) days with a minimum of seven (n=7) replicate LFB analyses. Before conducting the initial OCDL, the OC-CAL-1 standard is used to estimate the starting concentration for the OCDL study. If DOC analyses are being performed, the low-level LFBs must be filtered according to procedure in Section 11.4 prior to analysis for the OCDL. If the instrument can easily detect the OC-CAL-1 standard, the analyst should lower the concentration to a level so that the LFB produces a signal 2 to 5 times the background noise level of the instrument. It is recommended that the LFB be fortified somewhere between 0.1 to 0.5 mg/L OC. All available instrument digits are carried for the OCDL calculation. After completion of the OCDL, the calculation is rounded up or down according to Standard Method 1050 B.[15] The final result is reported in units used for the TOC or DOC procedure and recorded to two significant figures in the instrument log book. Calculate the OCDL using the equation:

$$\text{Organic Carbon Detection Limit} = St_{(n-1,\ 1-alpha\ =\ 0.99)}$$

where:

$t_{(n-1,1-alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom (t = 3.14 for 7 replicates)
n = number of replicates, and
S = standard deviation of replicate analyses.

If the initial OCDL exceeds 0.35 mg/L or the mean recovery of the LFB used in the OCDL determination exceeds $\pm$ 50% of the true value, then the OCDL determination must be repeated.

9.3 INITIAL DEMONSTRATION OF CAPABILITY FOR DOC DETERMINATION

9.3.1 Perform Sections 9.2.1 through 9.2.4 as prescribed for TOC.

9.3.2 INITIAL DEMONSTRATION OF FILTER MEMBRANE SUITABILITY - Filter membranes are capable of affecting DOC and UVA analyses either by desorption (leaching) of DOC and UV-absorbing materials from the filters to

the samples, or by adsorption (uptake) of DOC and UV-absorbing materials from the samples onto the filters. Filter membranes selected for DOC and UVA measurements must not desorb nor adsorb significant DOC and UV-absorbing materials. Desorption is minimized by pre-washing selected filters as described in Section 9.3.2.2. Adsorption is minimized by filtering a portion of the sample to waste before sample collection as described in Section 9.3.2.3. Because the filtration of relatively turbid samples may cause filters to clog, pre-filtration may be necessary and pre-filter preparation is described in Section 9.3.2.1. Due to the possibility of lot-to-lot variations in the levels of contamination or adsorption, it is recommended that for each filter lot, the user determine the amount of LRW needed to wash the filters and the amount of sample that needs to be filtered and discarded prior to collection of filtrate (filter-to-waste volume). A minimum of three filters (from each new lot) should be cleaned and checked for desorption/adsorption prior to using the filters for actual samples. This evaluation must be repeated when filters are purchased from another manufacturer or when the type of filter being used is changed.

9.3.2.1 PRE-FILTER PREPARATION - If the analyst anticipates that the UVA and DOC sample will clog the 0.45-µm pore size filter membrane before enough filtrate can be collected, glass fiber pre-filters without organic binders may be used. Karanfil et al [10] suggested cleaning the pre-filter by heating to 550 °C for one hour, cooling to room temperature, then washing it with 500 mL of LRW. A 25-mL filter-to-waste volume (Sect. 9.3.2.3) was also recommended. The pre-filters must be demonstrated as acceptable using the procedures described below in Sections 9.3.2.2 and 9.3.2.3. Depending on the design of the filter apparatus, the analyst may be able to insert a pre-filter into the filter apparatus. The pre-filter and filter apparatus could then be washed as a unit, following the procedure in Section 9.3.2.2. Prefilter adsorption and desorption may also be tested separately from the filter membrane.

9.3.2.2 FILTER CLEANING - UV-absorbing materials and DOC are removed from the filter and filter apparatus by passing LRW through the filter. The volume of LRW required depends on the type and disc size of the filter. For the filter apparatus used to generate the data in this method, three successive rinses of 250 mL each (for a total of 750 mL) removed UV-absorbing materials and DOC that could leach from the filter and apparatus. (The Karanfil [10] study found that a 500 mL wash was sufficient to prepare the 47-mm disk filters recommended in their study for DOC samples and a wash of 100 mL was sufficient for filters used solely to prepare UVA samples.) Acceptable cleaning is demonstrated by analyzing filter blanks (Sects. 11.4.3, 11.6) and meeting the criteria

in Section 9.9. The volume of LRW required to obtain acceptable filter blanks is then used to clean filters for analyses of all samples (Sect. 11.4). Filters that cannot be cleaned to meet the referenced criteria must not be used in the preparation of DOC and UVA samples.

9.3.2.3 FILTER-TO-WASTE VOLUME DETERMINATION - In order to minimize the loss of sample onto the filter by adsorption, a portion of the sample must be used to saturate the adsorption sites on the filter after it is cleaned according to Section 9.3.2.2. The amount of sample filtrate that must be discarded prior to collecting filtrate for DOC and/or UVA analyses will vary depending upon the type and size of filter and the volume should be minimized in order to prevent filter clogging. A 25-mL filter-to-waste volume was recommended when using the hydrophilic polyethersulfone and hydrophilic polypropylene filters of 47-mm disc size studied by Karanfil et al [10] based on evaluations using low-turbidity model waters prepared from preconcentrated humic and fulvic materials.

In this method, a low-turbidity (i.e., TOC = DOC) finished water sample can be used in the filter-to-waste determination. For laboratories that are analyzing samples from a variety of sources, the selected water should have a TOC concentration in the range of 1 to 3 mg/L. For laboratories that only analyze samples from one source, the selected water should be a finished water with the lowest TOC that is generally observed (NOTE: Depending on the quality of the source water, this could be water with a TOC concentration much higher than the 1 to 3 mg/L recommended for laboratories that are analyzing samples from a variety of sources.)

A series of at least three filtrates are collected in separate containers for the filter-to-waste volume determination. The volume of each filtrate is determined based on the minimum volume required to make an analytical determination. For example, if the DOC analysis requires 30 mL, then a series of at least three successive 30-mL filtrates should be collected. For UVA, three successive 10-mL filtrates can be collected. If DOC and UVA analyses are to be performed on the same filtrate, then the volume of each filtrate should be adjusted to provide the minimum volume necessary to accommodate both analyses (in the above example, three successive 40-mL washes).

Each filtrate is analyzed according to the procedure in Section 11 and the concentration is compared to the concentration of the unfiltered sample. When the concentration of the filtrate is within ± 15% of the concentration measured in the unfiltered sample, then the recommended

filter-to-waste volume is the sum of the volumes of that filtrate and any previous filtrates in the series. For example, if the unfiltered sample has a TOC concentration of 3.5 mg/L and the filtrate series (each filtrate = 30 mL) have concentrations of 2.3, 3.2, and 3.4 mg/L, then a minimum of 60 mL of sample should be filtered-to-waste prior to collecting filtrate for DOC analyses. It is recommended that the filter-to-waste volume be determined by performing this test on at least three filters from each lot and averaging the results. **Filters that require large volumes of filter-to-waste should be avoided**, because they will be more subject to clogging prior to the collection of the necessary volume of filtrate for analysis. The filter-to-waste volume that is determined in this section must be used in the filtration procedure described in Section 11.4.4.

9.3.3 Perform Sections 9.2.5 through 9.2.7 using filtered LFBs. The LFBs must be prepared using the same procedure used to prepare samples (Sect. 11.4).

9.4 INITIAL DEMONSTRATION OF CAPABILITY FOR UVA DETERMINATION

9.4.1 INITIAL CHECK OF SPECTROPHOTOMETER PERFORMANCE - The UV Spectrophotometer must be checked annually for 0 % transmittance, wavelength accuracy, stray radiant energy, accuracy and linearity, and optical alignment. It is recommended that the instrument performance be verified through the manufacturer or a scientific instrument service company. If independent verification of performance is not feasible, the laboratory may acquire a certified spectrophotometric filter set and conduct the evaluation. Wavelength verification is made using certified spectrophotometric filter sets with values traceable to NIST. Using the filter set, test two wavelengths between 220 and 340 nm. The instrument performance should be recorded in the instrument log and be used to monitor the spectrophotometer performance over time. Follow the instrument manufacturer's operation manual when measuring the acceptable wavelength transmittance limits.

9.4.2 Verify the spectrophotometer performance according to the procedure as outlined in Section 10.4.

9.4.3 Conduct the filter membrane suitability study described in Section 9.3.2 for UVA.

9.5 CONTINUING CALIBRATION CHECK (CCC) - With each analysis batch, analyze a Low-CCC at or below the MRL (Sect. 9.10) prior to TOC or DOC sample analysis. Subsequent CCCs are analyzed after every ten samples and after the last sample. The concentrations should be rotated to cover the instrument calibration range. A Mid-CCC is required during every analysis batch. Acceptance criteria are as follows: Low-

CCC, ± 50% of true value; Mid-CCC, ± 20% of true value; High-CCC, ± 15% of true value, see Section 10.3 for concentrations.

9.6 FIELD DUPLICATE (FD) - Within each analysis batch, a minimum of one set of field duplicates must be analyzed (FD1 and FD2). Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Duplicate sample analyses serve as a check on sampling and laboratory precision. Two samples are collected at the field site and are treated exactly alike.

9.6.1 Calculate the relative percent difference (RPD) for duplicate measurements (FD1 and FD2) using the equation:

$$RPD = \frac{|FD1 - FD2|}{(FD1 + FD2)/2} * 100$$

9.6.2 Relative percent difference for field duplicates having an average concentration of ≥ 2 mg/L OC should fall in the range of ≤ 20% RPD. If field duplicates in this concentration range exhibit an RPD greater than 20%, results should be flagged and the cause for the greater difference (e.g. incomplete IC removal or matrix interference), investigated. UVA readings should be ≤ 10% RPD. NOTE: *Greater variability may be observed for samples with OC approaching the OCDL.*

9.7 LABORATORY FORTIFIED BLANK (LFB) - Within each DOC analysis batch, analyze an aliquot of reagent water or other blank matrix which has been fortified with KHP at a concentration of 1-5 mg/L OC. Recovery for the LFB must be within ±20% of the true value. One LFB is required with each DOC analysis batch. For the DOC analysis, an LFB is subjected to the same preparation and analysis as a sample, including filtration (Sect. 11.4). The LFB is not determined for the TOC or UVA measurements.

9.8 LABORATORY FORTIFIED MATRIX (LFM) - Within each TOC or DOC analysis batch, an aliquot of one field sample is fortified with an aliquot of the OC-PDS (Sect. 7.8.3). The spike concentration used should result in an increase in the LFM concentration of 50 to 200% of its measured or expected concentration. Over time, samples from all routine sample sources should be fortified. For DOC analysis, the LFM is filtered prior to acidification and analysis.

9.8.1 Calculate the percent spike recovery (%REC) using the equation:

$$\%REC = \frac{(A - B)}{C} * 100$$

where
A = measured concentration in the fortified sample
B = measured concentration in the unfortified sample, and
C = fortification concentration.

9.8.2 Recoveries may exhibit a matrix dependence. If the LFM recovery falls outside of 70 to 130% for any fortified concentration, the analyst should suspect that inorganic carbon was not properly removed (Sect. 11.5) from the sample or that contamination or matrix interference exists (Sect. 4) and can not be removed. If the source of the poor recovery can not be identified, the analyst should label the sample report "suspect/contamination or matrix interference" to inform the data user that the sample data quality is questionable but should not be rejected. Failure to meet the recovery criteria after repeated sampling may suggest that the sample matrix may need further study.

9.9 LABORATORY REAGENT BLANK (LRB) AND FILTER BLANK (FB) - Within each analysis batch, a minimum of one LRB must be analyzed. For DOC and UVA analysis, the FB serves as the LRB. If more than one lot of filters is used in a DOC or UVA analytical batch, a FB must be analyzed for each lot. The analyst should be aware that additional filter blanks, up to one for each sample, are required by some regulations (e.g., *40 CFR 141.131(d)(4)(i)*).

The LRB or FB is used to assess contamination from the laboratory environment and background contamination from the reagents used in sample processing and is treated exactly the same as a sample. The volume of the FB must be the same as the sample volume. If UVA is to be determined, the FB (UVA-FB) must have an absorbance of ≤ 0.01 cm^{-1} UVA. The LRB and/or the FB (DOC-FB) must be ≤ 0.35 mg/L OC. If 0.35 mg/L OC or 0.01 cm^{-1} UVA is exceeded, background carbon or reagent contamination should be suspected. The cause for significant changes in the LRB or FB value must be identified and any determined source of contamination must be eliminated. For the FB, this may mean redetermination of filter membrane suitability (Sect. 9.3.2). The cause of the contamination and the corrective action used to remedy the problem is then recorded in the instrument log for future reference.

9.10 MINIMUM REPORTING LEVEL (MRL) - The OCDL should not be used as the MRL. For TOC analysis, it is recommended that an MRL be established no lower than the mean LRB measurement plus 3σ, or two times the mean LRB measurement, whichever is greater. For DOC analysis, the FB is substituted for the LRB. This value should be calculated over a period of time, to reflect variability in the blank measurements. **Although the lowest calibration standard for OC may be below the MRL, the MRL for OC must never be established at a concentration lower than the lowest OC calibration standard.**

9.11 QUALITY CONTROL SAMPLE (QCS) - During the analysis of the IDC (Sects. 9.2, 9.3), each time new OC-PDS solutions are prepared (Sect. 7.8.3), or at least quarterly, analyze a QCS from a source different from the source of the calibration standards. The QCS is used to provide an independent verification of the method and the TOC instrument system. To verify the stock or calibration solutions by comparison with the QCS, dilute the calibration solution and QCS to a concentration in the mid range of the calibration curve (approx. 1 - 5 mg/L TOC) in the same manner that the OC-CAL standards are made (Sect. 7.8.4). Acceptable verification of the calibration is made when the means of 3 analyses for both the calibration solution and QCS, having a concentration range between 1 to 5 mg/L OC, agree to within ±20% of the true value. If the measured QCS concentration is not within ±20% of the true value, the calibration solution must be remade and/or the source of the problem must be determined and corrected. Analysis of the QCS only applies to TOC and DOC determination.

9.12 SPECTROPHOTOMETER CHECK REQUIREMENT - The performance of the spectrophotometer is initially demonstrated using the procedure in Section 9.4.1. The day-to-day performance of the spectrophotometer is checked using KHP-SCS (Sect. 7.10) or a commercially available SCS (COMM-SCS, Sect. 7.9) according to the procedure in Section 10.4.

10.0 CALIBRATION AND STANDARDIZATION

10.1 INSTRUMENT SET UP AND OPTIMIZATION - Prior to calibrating the TOC instrument, clean the instrument system with carbon dioxide free water and sparge reagents with ultra high purity reagent gas as specified by the instrument manufacturer to remove background carbon dioxide. NOTE: *TOC Instrument 1 does not require reagent gas for operation*. Monitor the instrument background carbon dioxide levels for at least 30 minutes or until the background signal reaches the manufacturer's recommended level. The instrument should have a stable background and be free from drift caused by CO_2 contaminated gas or leaks in the system. Adjust instrument temperature, reagent gas and reagent pump flow settings according to the manufacturer's operation manual. Some instruments may require reagent priming runs to clean the flow injection system and reduce carbon background. After the instrument is judged to be stable, load the auto-injector or prepare to manually inject four LRB samples and start the analysis. The data collected from the first injection of LRB is discarded and is considered a system cleanup blank. The next three LRB injections should produce consecutive readings that fall within 20% of their mean. If these conditions are met, the instrument is ready for calibration. If not, use the OC-CAL-1 standard and repeat this section. If the three injections of OC-CAL-1 do not produce consecutive readings that fall within 20% of their mean, the instrument is not ready to operate and maintenance must be performed according to the instrument operation manual before proceeding.

10.2 CALIBRATION CURVE - A new calibration curve is generated when fresh standards are made (Sect. 7.8.4) or when CCCs fall out of QC limits (Sect. 10.3). Use a CB and at least four OC-CAL standards that span the concentration range of the samples to be analyzed. For example, if the samples to be analyzed are low in concentration (a range falling between 0.5 to 5 mg/L OC), prepare a calibration blank and a minimum of four TOC calibration standards (CB, OC-CAL 1 - 4, see Sect. 7.8.4). The lowest concentration calibration standard must be at or below the MRL, which may depend on system sensitivity. Add an additional 40 µL of H_3PO_4, HCl, or H_2SO_4, depending upon instrument requirements (Sect. 8.0), to the 40-mL injection vial(s). Sparge the calibration standards using the IC removal procedure in Section 11.5 prior to calibrating the instrument. Inject the standards from low to high concentration and calibrate the instrument. Be careful not to extend the calibration range over too wide of a concentration range as flow injection memory may cause analytical error (Sect. 9.2.3). The optional OC-CAL 6 - 7 may be used when operating the instrument in a higher concentration range.
NOTE: *For instruments that have an internal calibration setting, the calibration is checked by comparing the five point calibration curve with the internal calibration point. If the five point calibration curve does not agree with the internal calibration using the CCC criteria in Section 10.3, the internal calibration of TOC instrument must be reset by the manufacturer or adjusted by the analyst, following the manufacturer's operation manual.*

10.2.1 With the instrument in the ready mode, initiate the automated instrument calibration routine as per the instrument manufacturer's operation manual. The computer generated calibration curve must have $r^2 \geq 0.993$ before proceeding with analyses. Ideally the instrument calibration should be $r^2 \geq 0.9995$ for best results. After the instrument system has been calibrated, verify the calibration using the Continuing Calibration Check (CCC, Sect.10.3) and QCS (Sect. 9.11).

10.2.2 Save the data from the initial calibration curve and record it in the laboratory notebook or instrument log. The initial calibration curve serves as a historical reference so that future calibrations curves can be compared to determine if the slope or sensitivity of calibration has changed. If the slope or sensitivity of the instrument changes such that QC requirements cannot be met, consult the instrument manual or lab SOP for corrective action, which may include instrument maintenance and recalibration.

10.3 CONTINUING CALIBRATION CHECK (CCC) - Demonstration and documentation of continuing calibration is required and must meet the requirements listed below. The CCC solutions are made up weekly or just prior to a sample run and are prepared in the same manner as the OC-CALs (Sect. 7.8.4). An analysis batch begins with the analysis of a Low-CCC. CCCs are analyzed every 10 samples and must also include a

Mid-CCC. Subsequent CCCs should alternate between low, medium, and high concentrations, and must end the analysis batch. In summary, at least one Low-CCC and one Mid-CCC is analyzed with each analysis batch in order to verify the calibration curve. It is recommended that low, mid, and high CCCs be used to verify the calibration curve over time.

10.3.1 **Low-CCC** - the concentration range may vary from as low as 2 times the OCDL up to 0.7 mg/L OC. The Low-CCC is used to verify the low end of the calibration and must be at or below the MRL, which may depend on system sensitivity. The recovery for the Low-CCC must be within $\pm$ 50% of the true value.

10.3.2 **Mid-CCC** - the concentration is varied between 1.0 mg/L to 5.0 mg/L OC. The purpose of this CCC is to verify the precision and accuracy at the calibration range where critical source water treatment decisions are made. The Mid-CCC concentration may be varied to meet changing regulatory requirements. The Mid-range CCC must be within ±20% of the true value. If it is not, the TOC instrument system must be recalibrated.

10.3.3 **High-CCC** - the concentration range is varied between 5 to 50 mg/L OC. The selection of the High-CCC should be near the concentration of the highest OC-CAL standard used. The purpose of this CCC is to bracket the concentration the samples that are typically analyzed and to verify the upper range of the calibration curve. High-CCC must be within ±15% of the true value. If it is not, the TOC instrument system must be recalibrated.

10.4 SPECTROPHOTOMETER PERFORMANCE CHECK - The performance of the spectrophotometer is initially demonstrated using the procedure in Section 9.4.1. The day-to-day performance of the spectrophotometer is checked using KHP-SCS (Sect. 7.10) or a commercially available SCS (COMM-SCS, Sect. 7.9) prior to analyzing any UVA samples using the procedure described below.

10.4.1 Using a transfer pipet fill the spectrophotometer cell with the COMM-BKS or KHP-SCS-BLANK (Sects. 7.9.1, 7.10.1). Use this solution to zero the spectrophotometer.

10.4.2 After the spectrophotometer is zeroed, empty the cell, clean with LRW, rinse with methanol, dry with N_2 or reagent grade air, and fill it with the KHP-SCS or COMM-SCS.

10.4.3 Read the UVA of the KHP-SCS or COMM-SCS. The reading must be within 10% of the expected absorbance value. Record the absorbance of the KHP-SCS or COMM-SCS in the spectrophotometer instrument logbook. Empty the

cell, clean with LRW, rinse with methanol, and dry with N_2 or reagent grade air.

10.4.4 If the SCS absorbance criteria stated above cannot be met, discard the COMM-SCS or the KHP-SCS and purchase new COMM-SCS or remake the KHP-SCS. Repeat Section 10.4.

11.0 PROCEDURE

11.1 TOC/DOC SAMPLE INTEGRITY EVALUATION - It is important to analyze a TOC or DOC sample as directly and as soon as possible. Sample handling and preparation should be minimized. Upon receiving the sample from the field, the analyst must determine if the sample was treated and stored according to instructions found in Section 8.

11.2 OPTIONAL TREATMENT FOR TOC/DOC SAMPLE MATRIX LOSS - Aquatic humic substances precipitate at pH below 2 [16], and may move to glass vessel walls or instrument tubing. If the analyst suspects that humic substances have precipitated (which sometimes occurs in blackwaters)[14] or flocked to the bottom of the sample container, the sample is degassed by sparging to remove IC as directed in Section 11.5. The sample is then split into two portions. One portion is left at a pH $\leq$2, and the pH of the second portion is adjusted to pH 5 to 7 in order to increase the solubility of hydrophobic matter in the sample. Both samples are allowed to sit capped for ½ hour before further sample processing. These samples are treated in the same manner as field duplicates (FD), Section 9.6. The results of both split samples and corresponding pH values should be reported to the data user.

11.3 TOC SAMPLE PREPARATION - Remove the TOC sample from cold storage and allow the sample to come to room temperature. Determine if the sample has been preserved by acidification to a pH $\leq$2 by placing some drops on pH paper or by pouring some of the sample into a small beaker and checking it with a glass or solid-state pH electrode. **Do Not** put the pH paper or electrode into the sample bottle. If the pH is greater than 2, discard the sample.

11.3.1 TYPICAL TOC SAMPLE PRE-TREATMENT - Samples that appear to be low in particulate and suspended material are generally transferred directly to the 40-mL injection vial. If the sample appears to contain sediment or floating material, allow the sample to sit for a minute or two to allow sediment material to settle back to the bottom of the bottle. After allowing the sample to settle, transfer the sample from the middle of the bottle using a disposable pipet to the injection vial. Add 40 µL of H_3PO_4, HCl, or H_2SO_4 depending upon instrument requirements (Sect. 8.0) to the 40-mL injection vial and label it.

11.3.2 Proceed to Section 11.5, for IC removal.

11.4 SUVA SAMPLE PREPARATION - If SUVA is not being determined, proceed to Section 11.5. The SUVA determination consists of paired sample analyses composed of a DOC sample and a UVA sample. DOC and UVA samples may be taken from the same bottle, or may be taken from separate field duplicate bottles. Remove the DOC and UVA sample(s) from cold storage and allow them to come to room temperature. The laboratory is required to document any use of alternative filters, apparatus (see note, Sect. 6.1), or changes in the SUVA sample preparation procedure. All QC requirements (Sect. 9) must be met.

11.4.1 Samples for DOC and UVA analysis are NOT acidified in the field. The DOC sample is acidified after filtration as described below and the UVA sample is not acidified at all. Determine if the sample(s) was accidentally preserved by placing a few drops from the sample on pH paper or by pouring some of the sample into a small beaker and checking it with a glass or solid-state pH electrode. **Do Not** put the pH paper or electrode into the sample bottle. Placing the pH paper or electrode into the sample bottle will contaminate the sample solution with organic carbon. If this happens, the sample must be discarded. If the UVA sample pH is ≤ 2, check to make sure that the sample is actually for the UVA determination. It is possible that this sample is a TOC or filtered DOC sample and was mislabeled as a UVA sample. If the sample set was not mislabeled or switched but accidentally preserved, the sample must be discarded. The analyst must check the date and time of collection to ensure that the sample holding times listed in Section 8.1 have been met.

11.4.2 Filter Cleaning - Cleaning the filter apparatus, including the filter, removes trace organic compounds that may have been left behind in the manufacturing process. This cleaning must be done immediately prior to sample filtration. Rinse the filter with LRW, using the cleaning procedure used to determine filter membrane suitability (Sect. 9.3.2.2), including the cleaning of the pre-filter if a pre-filter is necessary.

11.4.3 Filter Blank (FB) - Use a clean filter apparatus (prepared in Sect. 11.4.2) and filter an aliquot of LRW into an injection vial for the DOC analysis and another aliquot of LRW into a vial for UVA analysis (Figure 1). FB volume must be the same as the sample volume collected in Section 11.4.4. During the development of this method, approximately 250 mL of LRW was filtered and aliquots were poured into two 40-mL injection vials and labeled as the DOC and UVA FBs. If the DOC and UVA analyses are coming from two separate bottles, a filter apparatus will be needed for each bottle and an FB should be prepared from each apparatus. Add 40 µL of H_3PO_4, HCl, or H_2SO_4 (as required by the various instrument types, Sect. 8.0) to the 40-mL DOC-FB injection vial. **Do not acidify** the UVA-FB injection vial. These vials are paired with the respective SUVA sample and retained for DOC-FB and UVA-FB analyses.

11.4.4 Sample Preparation - Reassemble the filter apparatus. Pour enough sample onto the filter to saturate any adsorption sites, as determined according to the filter-to-waste procedure in Section 9.3.2.3. Apply vacuum until no visible water remains on the filter. Remove the vacuum, swirl the apparatus with sample filtrate, disassemble, and discard the sample filtrate rinse. Reassemble the filter apparatus and pour an additional aliquot of sample into the top of the filter apparatus. Attach the vacuum and retain the filtrate. Pour one aliquot into a 40-mL injection vial and label it to identify it as the DOC sample. Pour a second aliquot into a 40-mL injection vial and label it to identify it as the UVA sample. Add 40 µL of H_3PO_4, HCl, or H_2SO_4 to the 40-mL DOC injection vial. **Do not acidify** the UVA injection vial. As with the DOC and UV FBs (Sect. 11.4.3), separate filter apparatus may be used for the DOC and UVA samples, in which case the filtrate need not be split into two aliquots. For a sample that is difficult to filter, an additional filter apparatus or the optional pre-filter insert apparatus may be used. The use of additional filters may require the collection of additional FBs, collected as specified in Section 11.4.3. The resulting additional DOC-FB, UVA-FB sample filtrates are collected, their volumes composited and then placed into their respective injection vials.

11.5 INORGANIC CARBON REMOVAL - **All OC-CALs, TOC and DOC samples, DOC-FBs, and LRBs must be treated to remove IC prior to OC analysis. UVA samples and UVA-FBs are <u>not</u> sparged with nitrogen gas or otherwise treated to remove IC prior to analysis** (See Figure 2). The laboratory is required to document any use of alternative IC removal apparatus (Sects. 6.9, 11.5.2) or changes in the IC removal procedure. All quality control requirements (Sect. 9.2.4) must be met. NOTE: *If a sparging apparatus is used, it should be isolated from the organic laboratory and be free of organic contaminants.*

11.5.1 CLEANING SPARGING APPARATUS: Before initial use and immediately after each use, the sparging apparatus must be cleaned. With the nitrogen turned off, dip the stainless steel needles in a 40-mL injection vial containing dilute acid (40 µL H_3PO_4, HCL, or H_2SO_4 per 40 mL LRW). Take the needles out of the dilute acid and turn the nitrogen back on to flush out any residual dilute acid. If disposable pipettes are used as part of the sparging apparatus, discard the pipettes after each use instead of attempting to clean and reuse them.

11.5.2 SPARGING PROCEDURE: Submerge the apparatus needles used to sparge the samples near the bottom of the 40-mL sample injection vial. Data generated for this method were generated by externally sparging the acidified samples with nitrogen gas, at 100 to 200 mL/minute, for 20 minutes per 40-mL sample injection vial. Some instrument companies provide optional inorganic

carbon removal apparatus that may produce an efficient means for the removal of IC. The laboratory must demonstrate sparging efficiency by the performance of the IC removal sparging efficiency test (Sect. 9.2.4) and meeting the LRB requirements as stated in Section 9.9.

11.6 SAMPLE ASSAY

11.6.1 TOC/DOC Sample Analysis - This is accomplished by placing into the injection vial tray a series of 40-mL injection vials usually containing any or all of the following types of samples: LRB, DOC-FB, CB, OC-CAL(s), CCC s (Low, Mid or High concentration), field samples, FD1 & FD2, LRB between samples if needed as specified in Section 9.2.3, LFB, LFM, and the QCS. The DOC-FB maximum allowable background concentration is 0.35 mg/L OC. The injection tray is placed into the instrument, the run is initiated, and the results of analyses are recorded.

11.6.2 UVA ANALYSES - If the spectrophotometer performance meets the SCS absorbance criteria as stated in Section 10.4, fill the cell with LRW and zero the instrument. Rinse and fill the cell with LRW from a second source. Verify UVA ≤ 0.01 cm^{-1} for second source LRW. Next fill the cell with the UVA-FB and read the absorbance. The UVA-FB's maximum allowable background absorbance is 0.01 cm^{-1} UVA. If 0.01 cm^{-1} UVA for the UVA-FB is exceeded, the cause must be identified and any determined source of contamination must be eliminated. The spectrophotometer performance must then be rechecked (Sect. 10.4). The laboratory should also check the initial zero each time 10 samples have been read. Rinse the spectrophotometer cell with a small amount of the UVA sample or UVA-FB by directly pipetting or pouring the sample into the spectrophotometer cell and discarding the rinse. Refill the spectrophotometer cell, carefully clean the cell window, and place in the spectrophotometer cell holder. Alternatively, flow cells maybe used, filled and flushed as needed. Measure the UVA and record. If field duplicates are collected, the FD1 & FD2 sample filtrates are also read and recorded.

12.0 DATA ANALYSIS AND CALCULATION

12.1 TOC DIRECT READING: The TOC concentration is calculated by the automated instrument system's software. Follow the instrument manufacturer's operation manual when making instrument response adjustments for instrument system blank corrections. The TOC calculation assumes that the sample has been properly preserved, that only a trace amount of IC remains following the IC removal procedure, and that any remaining IC will not contribute to the TOC measurement and result in a calculation error. Some instrument systems calculate TOC from the difference of the total carbon (TC) minus the IC. The analyst is reminded that the IC in the sample is removed prior to sample analysis. Therefore, the reported TC is equal to, and the same

as, the TOC value (TOC =TC) and is read directly from the instrument's computer or printout.

12.2 SUVA CALCULATION: Follow the instrument manufacturer's operation manual instructions when making instrument response adjustments for instrument system blank correction. As in the above TOC calculation, the analyst is reminded that the IC of the DOC sample is removed prior to analysis. After filtration, the TOC instrument value is equal to the DOC. The SUVA is then calculated from the DOC & UVA data that results from the procedure as described above (Sects. 11.6.1, 11.6.2). The UVA of the sample in cm^{-1} is divided by the DOC of the sample, multiplied by 100 cm/M and either reported in units of L/mg-M or as "SUVA". The SUVA is calculated as follows:

SUVA (L/mg-M) = UVA(cm^{-1}) / DOC (mg/L) * 100 cm/M

UVA Calculation: UVA = A /d

where:

UVA = The calculated UV absorbance of the sample in absorbance units (cm^{-1}).

A = The measured UV absorbance at 254 nm of the sample that is filtered through a 0.45-µm filter media.

d = The quartz cell path length in cm.

NOTE: *A Filter Blank (FB) is used to monitor background carbon contamination (Sect. 11.4.3) and is not subtracted from the DOC and UVA measurements.*

12.3 Calculations should utilize all available digits of precision, but final reported concentrations should be rounded to two significant figures (one digit of uncertainty). The final calculation is rounded up or down according to Standard Method 1050B.[15]

13.0 METHOD PERFORMANCE

NOTE: *Data presented in Section 17 are from single-laboratory determinations. All available digits were used for calculation and the calculations were rounded prior to entry in the tables. The data were reported to as many as three significant figures to give the reader a better understanding of method performance.*

13.1 Table 17.1 summarizes the 3-day organic carbon detection limit (OCDL) study for five TOC instruments systems. The DOC determination ranged from 0.02 to 0.08 mg/L OCDL and the TOC determination ranged from 0.04 to 0.12 mg/L OCDL. All source

water samples reported in Section 13 and the Section 17 Tables were sparged for 20 minutes to remove inorganic carbon interferences.

13.2 Table 17.2 and associated sub-tables illustrate the single instrument precision and accuracy for each of the five TOC instrument technologies.

13.3 Tables 17.3 and 17.4 illustrate the instrument differences and performances for five TOC instruments analyzing seven different source water matrices.

13.4 In all cases, the TOC instruments had difficulty in analyzing the Saint Leon well water. The Saint Leon well water had a moderately high inorganic carbon content of approximately 100 mg/L IC, and a low organic carbon content of 0.2 to 0.6 mg/L OC. The Saint Leon well water organic carbon content was near the organic carbon detection limit. The low OC concentration produced the greatest differences between instrument responses. For low TOC samples with high IC, differences between instrument responses may be more apparent due to possible IC interference.

13.5 The TOC, DOC and SUVA procedures of this method are dependent on the operation manual for the TOC instrument system and the UV spectrophotometer as provided by the respective instrument manufacturers. However, all performance criteria and quality control requirements described in this method, as summarized in Tables 17.5 and 17.6, must be met.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036, (202)872-4477.

14.3 For recycle information, contact the US EPA, Pollution Prevention and WasteWise program, http://www.epa.gov/wastewise/ .

15.0 WASTE MANAGEMENT

15.1 The U.S. Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel*, available from the American Chemical Society at the address listed in Section 14.2.

15.2 The laboratory should consult with local authorities prior to disposal of any waste to publicly owned treatment works (POTW) and receive permission for that disposal.

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17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

17.1 ORGANIC CARBON DETECTION LIMIT (OCDL)[a]

Dissolved Organic Carbon (DOC), mg/L					
Instrument	**Fortified Conc.[b]**	**Mean Recovered Conc.**	**%RSD[c]**	**%REC[d]**	**OCDL**
1	0.130	0.155	11	119	0.054
2	0.125	0.116	22	93	0.082
3	0.250	0.249	4	100	0.035
4	0.130	0.125	5	96	0.018
5	0.250	0.233	9	93	0.068
Total Organic Carbon (TOC), mg/L					
Instrument	**Fortified Conc.**	**Mean Recovered Conc.**	**%RSD[c]**	**%REC[d]**	**OCDL**
1	0.130	0.159	14	122	0.071
2	0.125	0.145	26	116	0.118
3	0.250	0.259	8	104	0.061
4	0.130	0.130	9	100	0.036
5	0.250	0.251	7	100	0.059

[a] Organic Carbon Detection Limits were determined by analyzing 7 replicates over 3 days.
[b] LRW fortified as specified in the table.
[c] %RSD = percent relative standard deviation
[d] %REC = percent recovery

INSTRUMENT:
1: UV/Persulfate/Wet Oxidation with Permeation/Conductivity Detection
2: Elevated Temperature/Catalyzed/Persulfate/Wet Oxidation/Nondispersive Infrared Detection (NDIR)
3: UV/Low Temperature/Persulfate/Wet Oxidation/NDIR
4: Catalyzed/Combustion Oxidation(680 °C)/NDIR
5: High Temperature Combustion Oxidation/NDIR

17.2 SINGLE TOC INSTRUMENT PRECISION AND ACCURACY

17.2.1 TOC Instrument 1: UV/persulfate wet oxidation with permeation/conductivity detection

Dissolved Organic Carbon, mg/L[a]				
Source Water	Unfortified Sample Conc.		Fortified Sample Conc.	
	Mean	%RSD	Mean	%REC
Boulder Creek	1.63	1.62	12.2	105
Shingobee R.	2.98	0.19	13.5	105
Bolten Well	1.27	0.00	12.0	107
Ohio R. (Fernbank)	2.79	0.36	13.6	108
Muddy Creek	3.81	0.15	14.6	108
Great Miami R.	3.18	0.00	13.7	104
Saint Leon Well	0.53	0.97	11.0	104
Total Organic Carbon, mg/L[a]				
Source Water	Unfortified Sample Conc.		Fortified Sample Conc.	
	Mean	%RSD	Mean	%REC
Boulder Creek	1.73	0.33	12.1	103
Shingobee R.	3.16	0.18	13.0	98
Bolten Well	1.32	0.44	11.4	100
Ohio R. (Fernbank)	3.02	0.57	13.2	102
Muddy Creek	4.24	0.00	14.6	103
Great Miami R.	3.51	0.33	13.8	102
Saint Leon Well	0.66	0.52	11.1	104

[a] N = 3, samples fortified at 10mg/L OC using KHP

17.2 SINGLE TOC INSTRUMENT PRECISION AND ACCURACY, cont'd.

17.2.2 TOC Instrument 2: Elevated temperature/catalyzed/persulfate wet oxidation/NDIR

Dissolved Organic Carbon, mg/L[a]			
Source Water	**Unfortified Sample Conc.**	**Fortified Sample Conc.**	
	Mean	**Mean**	**%REC**
Boulder Creek	1.40	11.8	104
Shingobee R.	2.58	13.3	106
Bolten Well	1.04	12.6	105
Ohio R. (Fernbank)	2.41	13.3	108
Muddy Creek	3.25	14.3	110
Great Miami R.	2.68	13.4	107
Saint Leon Well	0.40	10.6	101
Total Organic Carbon, mg/L[a]			
Source Water	**Unfortified Sample Conc.**	**Fortified Sample Conc.**	
	Mean	**Mean**	**%REC**
Boulder Creek	1.38	11.2	98
Shingobee R.	2.62	12.7	100
Bolten Well	1.05	11.4	103
Ohio R. (Fernbank)	2.46	13.1	106
Muddy Creek	3.41	13.8	104
Great Miami R.	2.89	13.2	103
Saint Leon Well	0.38	10.5	102

[a] N = 2, samples fortified at 10mg/L OC using KHP

17.2 SINGLE TOC INSTRUMENT PRECISION AND ACCURACY, cont'd.

17.2.3 TOC Instrument 3: UV/low temperature/persulfate wet oxidation/NDIR

Dissolved Organic Carbon, mg/L[a]				
Source Water	Unfortified Sample Conc.		Fortified Sample Conc.	
	Mean	%RSD	Mean	%REC
Boulder Creek	1.52	1.81	11.5	100
Shingobee R.	2.71	1.10	13.2	104
Bolten Well	1.18	1.76	11.3	101
Ohio R. (Fernbank)	2.50	0.74	13.1	106
Muddy Creek	3.38	0.81	14.0	106
Great Miami R.	2.91	0.64	13.1	102
Saint Leon Well	0.56	0.88	10.7	101
Total Organic Carbon, mg/L[a]				
Source Water	Unfortified Sample Conc.		Fortified Sample Conc.	
	Mean	%RSD	Mean	%REC
Boulder Creek	1.47	1.77	11.2	97
Shingobee R.	2.72	0.02	12.7	99
Bolten Well	1.16	2.45	11.0	98
Ohio R. (Fernbank)	2.58	1.01	12.6	100
Muddy Creek	3.18	1.28	13.5	103
Great Miami R.	2.92	1.01	13.0	101
Saint Leon Well	0.45	1.57	10.7	102

[a] N = 3, samples fortified at 10 mg/L OC using KHP

17.2 SINGLE TOC INSTRUMENT PRECISION AND ACCURACY, cont'd.

17.2.4 TOC Instrument 4: Catalyzed, 680 °C combustion oxidation/NDIR

Dissolved Organic Carbon, mg/L[a]				
Source Water	Unfortified Sample Conc.		Fortified Sample Conc.	
	Mean	%RSD	Mean	%REC
Boulder Creek	1.54	5.75	11.4	98
Shingobee R.	2.71	3.18	12.4	97
Bolten Well	1.24	1.25	12.4	98
Ohio R. (Fernbank)	2.52	5.73	12.4	98
Muddy Creek	3.56	3.17	13.3	98
Great Miami R.	3.00	6.94	12.7	96
Saint Leon Well	0.38	27.4	10.1	98
Total Organic Carbon, mg/L[a]				
Source Water	Unfortified Sample Conc.		Fortified Sample Conc.	
	Mean	%RSD	Mean	%REC
Boulder Creek	1.46	2.86	11	100
Shingobee R.	2.84	2.19	13	97
Bolten Well	1.12	1.70	11	100
Ohio R. (Fernbank)	2.81	1.79	13	100
Muddy Creek	4.04	2.02	14	96
Great Miami R.	3.42	1.66	14	101
Saint Leon Well	0.28	7.64	10	100

[a] N = 3, samples fortified at 10 mg/L OC using KHP

17.2 SINGLE TOC INSTRUMENT PRECISION AND ACCURACY, cont'd.

17.2.5 TOC Instrument 5: High temperature combustion oxidation/NDIR

Dissolved Organic Carbon, mg/L[a]				
Source Water	Unfortified Sample Conc.		Fortified Sample Conc.	
	Mean	%RSD	Mean	%REC
Boulder Creek	1.21	1.18	11.0	98
Shingobee R.	2.29	1.15	12.0	97
Bolten Well	0.90	2.93	11.5	106
Ohio R. (Fernbank)	2.11	0.28	12.3	102
Muddy Creek	2.89	1.09	13.1	102
Great Miami R.	2.43	0.77	12.3	99
Saint Leon Well	0.38	27.4	10.0	96
Total Organic Carbon, mg/L[a]				
Source Water	Unfortified Sample Conc.		Fortified Sample Conc.	
	Mean	%RSD	Mean	%REC
Boulder Creek	1.26	6.02	11.0	97
Shingobee R.	2.45	0.84	12.1	97
Bolten Well	0.93	1.02	10.8	98
Ohio R. (Fernbank)	2.31	1.19	12.1	98
Muddy Creek	3.34	3.40	13.1	98
Great Miami R.	2.72	0.78	12.3	96
Saint Leon Well[b]	0.32	N/A	10.0	97

[a] N = 3, samples fortified at 10 mg/L OC using KHP
[b] N = 2 for this sample, N/A = not applicable

17.3 PRECISION AND ACCURACY DATA FOR DOC AND SUVA MEASURED IN SEVEN SOURCE WATERS ON FIVE INSTRUMENTS[a]

17.3.1 DOC Measurements for Seven Source Waters, Three Replicate Instrument Injections on Five Instruments

Dissolved Organic Carbon, mg/L, Unfortified Samples								
Source Water	**Inst #1**	**Inst #2**	**Inst #3**	**Inst #4**	**Inst #5**	**Mean**	**Std Dev**	**%RSD**
Boulder Creek	1.64	1.40	1.52	1.54	1.21	1.46	0.17	11
Shingobee R.	2.98	2.58	2.71	2.71	2.29	2.66	0.25	9
Bolton Well	1.27	1.04	1.18	1.24	0.90	1.13	0.15	14
Ohio R. (Fernbank)	2.79	2.41	2.50	2.52	2.12	2.47	0.24	10
Muddy Creek	3.81	3.25	3.38	3.56	2.89	3.38	0.34	10
Great Miami R.	3.18	2.69	2.91	3.00	2.43	2.84	0.29	10
St. Leon Well	0.53	0.40	0.56	0.38	0.25	0.42	0.13	30

17.3.2 DOC Measurements for Seven Source Waters, Fortified with KHP, Three Replicate Instrument Injections on Five Instruments

Dissolved Organic Carbon, mg/L, Samples Fortified at 10 mg/L OC									
Source Water	**Inst #1**	**Inst #2**	**Inst #3**	**Inst #4**	**Inst #5**	**Mean**	**Std Dev**	**%RSD**	**%REC[b]**
Boulder Creek	12.2	11.8	11.5	11.4	11.0	11.6	0.43	4	101
Shingobee R.	13.5	13.3	13.2	12.4	12.0	12.9	0.62	5	102
Bolton Well	12.0	11.5	11.3	11.2	11.5	11.5	0.31	3	104
Ohio R. (Fernbank)	13.6	13.2	13.1	12.4	12.3	12.9	0.54	4	105
Muddy Creek	14.6	14.3	14.0	13.3	13.1	13.9	0.62	5	105
Great Miami R.	13.7	13.4	13.1	12.7	12.3	13.0	0.55	4	102
St. Leon Well	11.0	10.5	10.7	10.1	10.0	10.5	0.40	4	100

[a] For instrument identification (by type) see Section 6.3.
[b] % Recovery calculated as described in Section 9.8.

17.3 PRECISION AND ACCURACY DATA FOR DOC AND SUVA MEASURED IN SEVEN SOURCE WATERS ON FIVE INSTRUMENTS[a], cont'd.

17.3.3 Mean SUVA Calculation Based on the DOC Data in 17.3.1 for Seven Source Waters

Source Water	UVA (cm^{-1})	SUVA [b] (L/mg-M)					
		Inst #1	Inst #2	Inst #3	Inst #4	Inst #5	Mean
Boulder Creek	0.0432	2.62	3.08	2.84	2.97 3	58 3.02	
Shingobee R.	0.0744	2.50	2.88	2.75	2.77 3	25 2.83	
Bolton Well	0.0236	1.86	2.28	2.01	1.91 2	62 2.14	
Ohio R. (Fernbank)	0.0727	2.60	3.01	2.90	2.88	3.43	2.97
Muddy Creek	0.1124	2.95	3.46	3.33	3.20	3.89	3.37
Great Miami R.	0.0895	2.81	3.33	3.07	3.05 3	69 3.19	
St. Leon Well	0.0077	1.46	1.93	1.38	1.83	3.13	1.95

[a] For instrument identification (by type) see Section 6.3.
[b] SUVA calculated as described in Section 12.2.

17.4 PRECISION AND ACCURACY DATA FOR TOC MEASURED IN SEVEN SOURCE WATERS ON FIVE INSTRUMENTS[a]

17.4.1 TOC Measurements for Seven Source Waters, Three Replicate Instrument Injections on Five Instruments

Total Organic Carbon, mg/L, Unfortified Samples								
Source Water	**Inst #1**	**Inst #2**	**Inst #3**	**Inst #4**	**Inst #5**	**Mean**	**Std Dev**	**%RSD**
Boulder Creek	1.73	1.38	1.47	1.46	1.26	1.46	0.17	12
Shingobee R.	3.16	2.62	2.72	2.84	2.45	2.76	0.26	10
Bolton Well	1.32	1.05	1.16	1.12	0.93	1.12	0.14	13
Ohio R. (Fernbank)	3.02	2.46	2.58	2.81	2.31	2.64	0.28	11
Muddy Creek	4.24	3.41	3.18	4.04	3.34	3.64	0.47	13
Great Miami R.	3.51	2.89	2.92	3.42	2.72	3.09	0.35	11
St. Leon Well	0.66	0.39	0.45	0.28	0.32	0.42	0.15	35

17.4.2 TOC Measurements for Seven Source Waters, Fortified with KHP, from Replicate Instrument Injections on Five Instruments

Total Organic Carbon, mg/L, Samples Fortified at 10 mg/L OC									
Source Water	**Inst #1**	**Inst #2**	**Inst #3**	**Inst #4**	**Inst #5**	**Mean**	**Std Dev**	**%RSD**	**%REC[b]**
Boulder Creek	12.1	11.3	11.2	11.4	11.0	11.4	0.43	4	99
Shingobee R.	13.0	12.7	12.6	12.5	12.1	12.6	0.32	3	98
Bolton Well	11.4	11.4	11.0	11.2	10.8	11.1	0.28	3	100
Ohio R. (Fernbank)	13.2	13.1	12.6	12.8	12.1	12.8	0.45	4	101
Muddy Creek	14.6	13.8	13.5	13.7	13.1	13.7	0.54	4	101
Great Miami R.	13.8	13.2	13.0	13.6	12.3	13.2	0.59	5	101
St. Leon Well	11.1	10.5	10.7	10.2	10.0	10.5	0.41	4	101

[a] For instrument identification (by type) see Section 6.3.
[b] % Recovery calculated as described in Section 9.8.

17.5 INITIAL DEMONSTRATION OF CAPABILITY (IDC) REQUIREMENTS (SUMMARY)

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sects. 9.2.1, 9.9	Initial Demonstration of Low System Background	Analyze LRB prior to any other IDC samples.	LRBs must be $\leq$ 0.35 mg/L OC and $\leq$ 0.01 cm^{-1} UVA.
Sects. 9.2.2, 9.11	Initial Calibration Verification	After initial calibration of TOC instrument system a QCS sample is used to verify accuracy.	The analyzed value of a 1-5 mg/L calibration standard must be within ±20% of the true value before proceeding with the method.
Sect. 9.2.3	Initial Organic Carbon Flow Injection Memory Check	Analyze after Low System Background requirement, but before any other TOC or DOC IDC samples.	LRB injections after the highest OC-CAL injection must be $\leq$ 0.35 mg/L TOC.
Sect. 9.2.4	Inorganic Carbon Removal	Prior to first analysis of samples and whenever the IC removal procedure is modified.	Analysis of the IC-TEST solution after IC removal must result in a concentration of $\leq$ 0.35 mg/L IC, measured as OC interference.
Sect. 9.2.5	Initial Demonstration of Accuracy	Analyze 5 replicate LFBs (at 2-5 mg/L OC).	The average recovery must be $\pm$20% of the true value.
Sect. 9.2.6	Initial Demonstration of Precision	Calculate precision of the accuracy samples.	The %RSD must be $\leq$ 20%.
Sect. 9.2.7	Organic Carbon Detection Limit (OCDL) Determination	Analyze 7 replicate LFBs over a period of at least 3 days at a concentration estimated to be near the DL.	The calculated OCDL must not exceed 0.35 mg/L. The mean recovery of the LFBs used in the OCDL determination must be $\pm$50% of the true value.

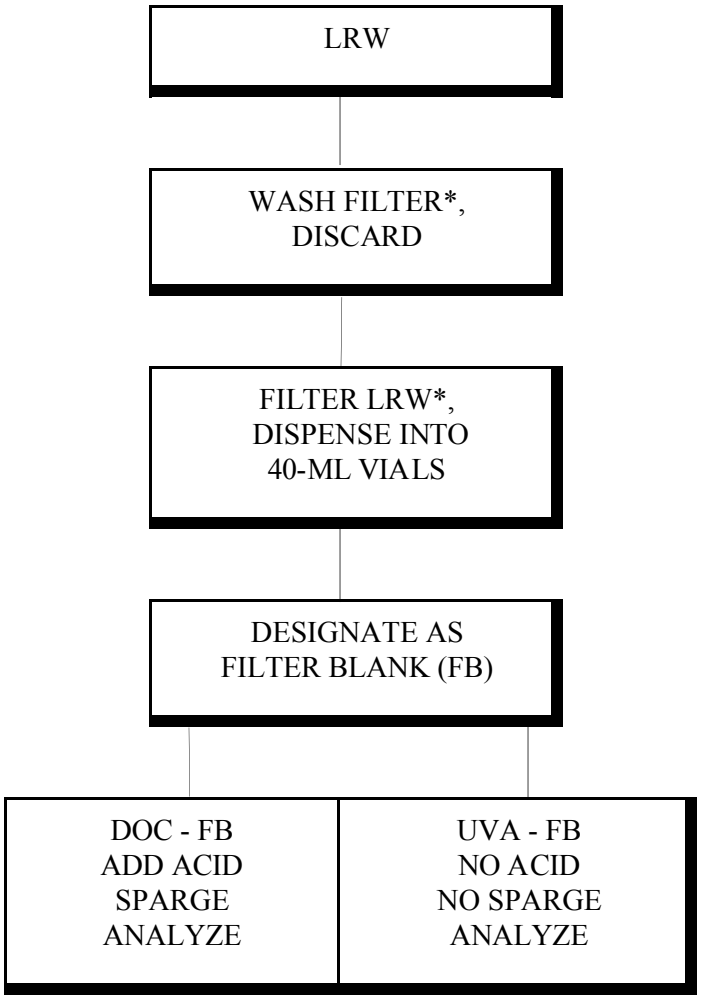
Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 9.3.2	Initial Demonstration of Filter Membrane Suitability	Prior to the first use of filters and whenever a manufacturer or filter type is changed.	FB $\leq$ 0.35 mg/L OC and/or $\leq$ 0.01 cm^{-1} UVA. Sample filtrate OC within $\pm$ 15% of unfiltered sample OC.
Sect. 9.4.1	Initial Spectrophotometer Check	Prior to first instrument use and annually thereafter.	Test two wavelengths between 220 and 340 nm. Check manufacturer's operation manual for acceptance limits.
Sects. 9.4.2, 10.4	Spectrophotometer Performance Check	Prior to analysis of samples.	UVA within 10% of expected absorbance value.

17.6 QUALITY CONTROL REQUIREMENTS (SUMMARY)

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 9.9	Blanks	One LRB with each TOC analysis batch. One FB with each DOC and UVA analysis batch.	TOC LRBs and DOC-FBs must be $\leq$ 0.35 mg/L OC. The UVA-FB must be $\leq$ 0.01 cm^{-1} UVA.
Sect. 8.1	Holding Time, SUVA	DOC - filtered and then acidified within 48 hours of collection. Analyzed within 28 days of time of collection.	Stored at $\leq$ 6 °C; preserved with acid to pH $\leq$ 2 after filtration.
		UVA - filtered and analyzed within 48 hours of time of collection.	Not preserved with acid, stored at $\leq$ 6 °C.
Sect. 8.2	Holding Time, TOC	TOC - analyze within 28 days from time of collection.	Preserved at pH $\leq$ 2 at the time of collection, stored at $\leq$ 6 °C.
Sects. 9.2, 9.3, 9.4	Initial Demonstration of Capability (IDC)	Performed whenever a new instrument is set up or when a new analyst is trained.	See Table 17.5.
Sects. 9.5, 10.3	Continuing Calibration Checks	Analysis of Low-CCC (at the MRL or below) at the beginning of each analysis batch. Subsequent CCCs analyzed after every 10 samples and after the last sample in the analysis batch, rotating concentrations to cover the calibrated range of the instrument. Mid-CCC required during each analysis batch.	Low-CCC: $\pm$ 50% of true value. Mid-CCC: $\pm$ 20% of true value. High-CCC: $\pm$ 15% of true value.

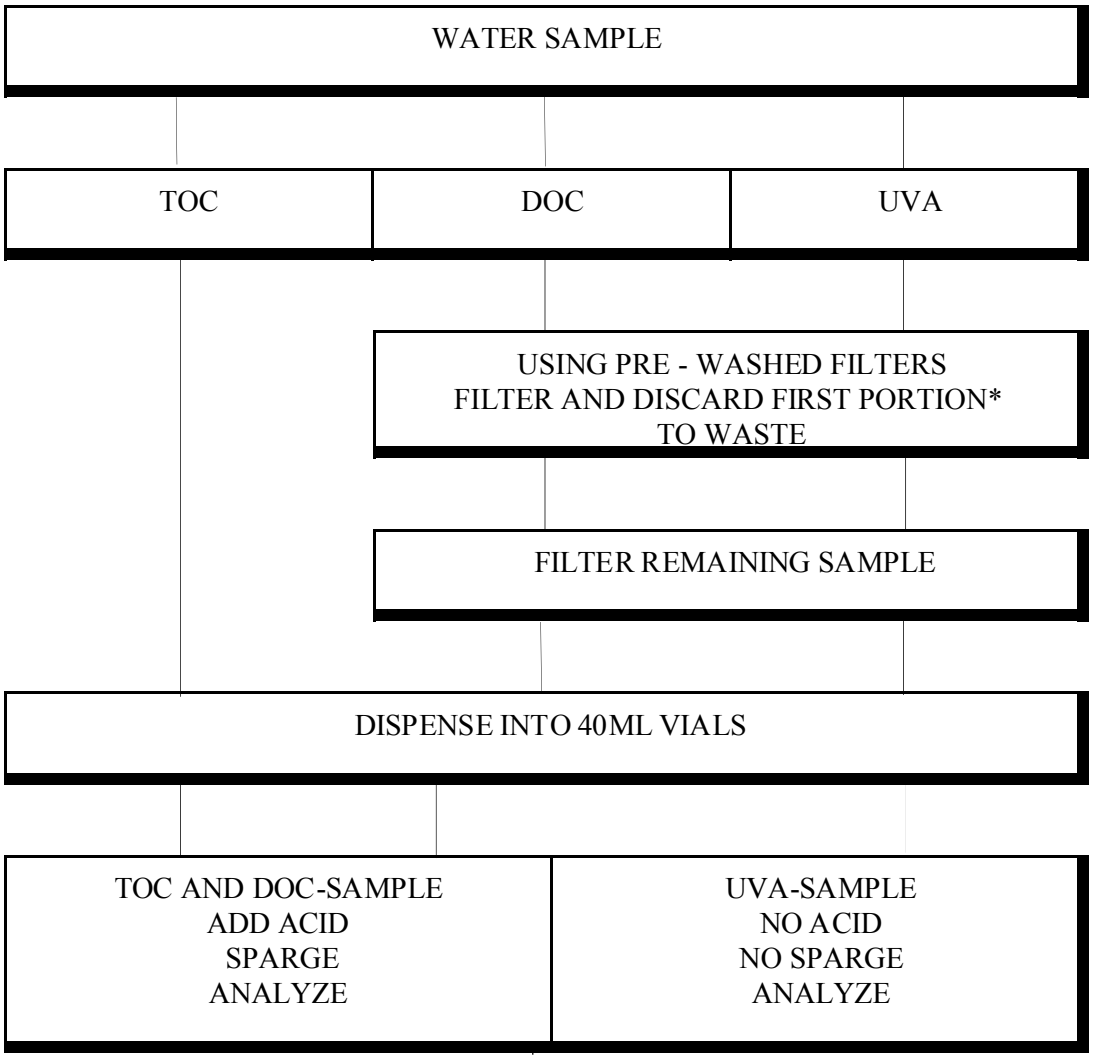
Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 9.6	Field Duplicate (FD) Analyses	One FD is collected and analyzed with each analysis batch.	FD > 2 mg/L OC < 20% RPD. UVA < 1 0% RPD.
Sect. 9.7	Laboratory Fortified Blank (LFB) analysis	One LFB is analyzed with every DOC analysis batch.	Concentration of 1-5 mg/L OC using KHP. Recovery must be within + 20% of true value.
Sect. 9.8	Laboratory Fortified Matrix (LFM)	One LFM is analyzed with every TOC or DOC analysis batch. Spike concentration should result in an increase in the LFM concentration of 50 to 200% of its measured or expected concentration.	Recovery outside 70-130% warrants investigation of matrix effect.
Sect. 9.11	Quality Control Sample (QCS)	The QCS is analyzed during the IDC, after each new calibration curve, each time new calibration solutions are prepared, or at least quarterly.	The analyzed value of a 1-5 mg/L QCS must be within ±20% of the true value.
Sec t. 10.2	Calibration Curve	A new calibration curve is generated when fresh standards are made and/or when CCCs are out of QC limits.	Calibration curve must have $r_2 > 0.993$ before proceeding with analyses.
Sect. 10.4	Spectrophotometer performance check	The day to day performance of the spectrophotometer is checked using the COMM-SCS and/or KHP-SCS prior to analyzing any UVA sample(s).	The UVA of the KHP-SCS or COMM-SCS reading must be within 10% expected absorbance values.
Sect. 11.6.2	Spectrophotometer Blank	A second source LRW is analyzed each time spectrophotometer is zeroed.	Analysis of second source LRW must result in UVA ≤ 0.01 cm^{-1}.

FIGURE 1: FILTER BLANK PREPARATION



*Using volume as determined in Section 9.3.2.

FIGURE 2 : SAMPLE PREPARATION



* Using volume as determined in Section 9.3.2.3.

415.3 - 56

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QUALITY ASSURANCE PROGRAM

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Policy Statement

The production of analytical data is never an end in itself. Analytical data are always associated with some kind of decision -making, whether it be to determine product compliance with established tolerances, to profile a pollutant in a segment of the environment, or to assess the health effects on humans. The data produced must be reliable evidence suitable for use in a court of law or sufficiently reliable to provide accurate assessments of the degree of pollution in some sector of the environment. Environment 1 Quality Assurance provides the framework for an Analytical Quality Control Program which insures that the final analytical data are truly valid and representative of the concentration profile for the matrix analyzed. The control of analytical performance in the laboratory is based on the assumption that a "valid sample" has been submitted for analysis. A "valid sample" implies that the sample was properly collected, adequately preserved, and delivered to the laboratory in a condition appropriate for all analytical techniques to be employed. Furthermore, the validity of controlled analytical performance is dependent upon the use of currently approved analytical methodology substantiated by the recording and reporting of subsequent laboratory results in a systematic and uniform fashion. It must be recognized, however, that quality control must begin with sample collection and not end until the resulting data are reported. The laboratory control of analytical performance is but one essential link in obtaining reliable data. A quality assurance effort will only be as good as the poorest, least-controlled area which has an effect on the resulting data.

CONTENTS

Page 4

Sample Validity

The majority of samples analyzed by Environment 1 (hereafter referred to as E1) are collected by the client while in some cases a member of the staff of E1 collects and delivers the samples.

Client Collection & Delivery

Whenever possible and when certain monitoring programs call for specific sample containers, E1 provides the containers to the client. Containers provided to the client arrive clean, of the proper material, marked with the requested test type, client ID#, client name and with the proper preservatives. If requested proper sample collection will be discussed with the client along with required shipment protocols. All sample containers provided for sample collection under the Safe Drinking Water Act are supplied with instructions for sample collection and shipment. Chain of Custody documentation is provided for all DWR (wastewater/groundwater) samples.

Laboratory Collection

Samples collected by the staff of E1 follow these protocols:

a) Adherence to required sampling methodology by either "grab" or "composite" collection as stipulated by a permit requirement or established regulatory requirements.

b) Use of sampling containers made of the proper materials, properly cleaned, labeled with the test type, client ID#, client name, and properly preserved.

c) Transportation of samples back to E1 in a timely manner to correspond with approved holding times.

d) Proper and complete COC documentation.

Page 5

Sample Receiving at the laboratory

Wastewater Samples. Sample temperatures are checked and documented upon arrival at the lab and must be 6.0C or less (and not frozen). Samples received with a temperature reading of less than 0.1C but are not frozen must have a notation recorded to this effect. Samples that are received within 1 hour of collection and do not meet the above criteria are acceptable if they show a downward trend in temperature from the time the samples were collected. Chemically preserved samples are check for proper preservation and documented. Sample container Chain of Custody is documented. Samples are rejected or qualified (at the request of the Permittee) if they do not meet proper criteria.

Drinking Water Samples. Sample temperatures are checked and documented upon arrival at the lab and must be 6.0C or less (and not frozen). Samples received with a temperature reading of less than 0.1C but are not frozen must have a notation recorded to this effect. Samples are rejected if they do not meet specifications for: proper containers, proper preservation, holding times, proper collection/transport, and completeness of the sample collection form. The lab may accept samples that have inaccurate or incomplete information on the collection form if the information can be verified with the water system in a timely manner.

Sample Tracking in the Laboratory

Each client of E1 has specific ID numbers based on the type of samples.

1-4999 ---------- Wastewater/Surface Water Monitoring (DWR)

5000-5999 ---------- Safe Drinking Water Act (miscellaneous parameters)

6000-6999 ---------- Landfill Groundwater/Leachate Monitoring

7000-9999 ---------- Safe Drinking Water Act

All sample containers are labeled with the following information: client name, client ID#, test type, location code, and date of arrival at the laboratory. Samples are then logged in by use of a computer program which stores the receiving data in the system. Chain of Custody Documentation (COC) is provided for all DWR samples arriving in the laboratory. The COC is checked for completeness and proper preservation is documented. A designated sample custodian delivers the samples to the appropriate analyst or places them in properly designated and maintained storage areas where they remain until analyzed. Analysts are responsible for completing the required analyses within proper holding times.

Page 6

Analytical Methodology

It is of the utmost importance that proper methodology be used for all samples which arrive at E1. Therefore, it is a requirement that the laboratory know exactly why the samples were collected and which regulatory program, if any, they fall within. Analyses using improper procedures may result in rejection of the data by regulatory authorities. The following sources are used by E1:

a) Standard Methods for the Examination of Water and Wastewater (current approved editions)
b) Methods for Chemical Analysis of Water and Wastes (EPA Manual, current approved editions)
c) Interim Radiochemical Methodology for Drinking Water, March 1976
d) SW 846 - Test Methods for Evaluating Solid Waste (current approved additions)
e) National Interim Primary Drinking Water Regulations
f) Custom designed methods for special, non-compliance projects

Common types of analyses include, but are not limited to:

a) various sample treatments (filtration, digestion, etc.)
b) specific electrodes
c) volumetric and gravimetric analyses
d) atomic absorption and colorimetry
e) ICP metals analyses
f) ICP/Mass Spec metals analyses
g) gas chromatography and GC/MS
h) HPLC analyses
i) bacteriological analyses
j) classical wet chemistries

Analyses are performed either by direct use of an established reference manual or step-by-step laboratory manuals which strictly adhere to reference sources. Any modifications are recorded and an explanation is listed. Special projects requiring custom analytical procedures use either client guidelines or incorporation of the best available technology.

All Standard Operating Procedures (SOPs) are to be reviewed annually and the date of the review is to be listed on the chart behind the method. The chart must also be completed if a revision to a method is made.

Page 7

SPECIFIC ANALYTE PARAMETERS

ANALYTE	DWR REPORTING LIMIT	LANDFILL REPORTING LIMIT	DRINKING WATER REPORTING LIMIT
ACIDITY	0 mg/l		0 mg/l
ALKALINITY	0 mg/l	0 mg/l	0 mg/l
BOD/CBOD	2 mg/l	2 mg/l	
BROMIDE	1 mg/l		
CHLORIDE	1 mg/l	1 mg/l	1 mg/l
CHLOROPHYLL A	1 ug/l		
COLOR, APPAR	5 Units		5 Units
CONDUCTIVITY	1 uMhos/cm	1 uMhos/cm	1 uMhos/cm
CYANIDE,TOTAL	0.005 mg/l	5 ug/l	0.050 mg/l
COD	20 mg/l	10 mg/l	
COLIFORM, MF	1 /100 mls		1 /100 mls
COLIFORM, MPN	2 /100 mls		2 /100 mls
COLILERT, P/A			"Absent"
COLISURE, P/A			"Absent"
COLITAG, P/A			"Absent"
ENTEROCOCCUS	1/100 mls		
FLUORIDE	0.10 mg/l		0.10 mg/l
HARDNESS	1 mg/l		1 mg/l
DETERGENTS,MBAS	0.02 mg/l		0.02 mg/l
AMMONIA NITRO.	0.04 mg/l		
NITRATE-NITRITE	0.04 mg/l		
NITRATE NITRO.	0.04 mg/l	0.04 mg/l	1.00 mg/l
NITRITE NITRO.	0.02 mg/l		0.02 mg/l
OIL & GREASE	5 mg/l		
PHOSPHORUS,TOT.	0.04 mg/l		0.04 mg/l
PHOSPHORUS,ORT.	0.01 mg/l		0.01 mg/l
PH	0-14 Units	0-14 Units	0-14 Units
PHENOL	5 ug/l		
SOLIDS,SETTLE.	0.1 ml/l		
SOLIDS,SUSPEND.	2.5 mg/l		
SOLIDS,T. DISS.	10 mg/l	10 mg/l	10 mg/l
SOLIDS, TOTAL	10 mg/l		
SULFATE	5 mg/l	250 mg/l	5 mg/l
SULFIDE	0.1 mg/l	1 mg/l	
TOC	1 mg/l		1 mg/l
TURBIDITY	1 NTU	1 NTU	1 NTU
TKN	0.20 mg/l		

- Lower reporting levels for some analytes may be obtained for special projects

Page 8

SPECIFIC ANALYTE PARAMETERS (METALS)

ANALYTE	DWR REPORTING LIMIT	LANDFILL REPORTING LIMIT	DRINKING WATER REPORTING LIMIT
ANTIMONY	3 ug/l	6 ug/l	3 ug/l
ARSENIC	5 ug/l	10 ug/l	5 ug/l
ALUMINUM	100 ug/l		
BARIUM	10 ug/l	100 ug/l	400 ug/l
BERYLLIUM	1 ug/l	1 ug/l	2 ug/l
CADMIUM	1 ug/l	1 ug/l	1 ug/l
CHROMIUM, TOTAL	5 ug/l	10 ug/l	20 ug/l
COBALT	10 ug/l	10 ug/l	
COPPER	10 ug/l	10 ug/l	50 ug/l
IRON	50 ug/l	300 ug/l	60 ug/l
LEAD	5 ug/l	10 ug/l	3 ug/l
MANGANESE	10 ug/l	50 ug/l	10 ug/l
MAGNESIUM	500 ug/l		1000 ug/l
MERCURY	0.2 ug/l	0.2 ug/l	0.4 ug/l
NICKEL	10 ug/l	50 ug/l	100 ug/l
SELENIUM	10 ug/l	10 ug/l	10 ug/l
SILVER	5 ug/l	10 ug/l	50 ug/l
THALLIUM	1 ug/l	5.5 ug/l	1 ug/l
TIN	100 ug/l	100 ug/l	
VANADIUM	10 ug/l	25 ug/l	
ZINC	10 ug/l	10 ug/l	50 ug/l
SODIUM	1000 ug/l		2500 ug/l
MOLYBDENUM	10 ug/l		
URANIUM			2 pCi/l
SILICA			500 ug/l
FERROUS IRON		200 ug/l	

* Lower reporting levels for some analytes may be obtained for special projects

Page 9

Facilities, Equipment, & Supplies

The offices and laboratories of Environment 1 are located within approximately 9,500 square feet. The following services are provided throughout the laboratory as needed:

a) ASTM Type II reagent grade water
b) Electrical service with constant voltage and dedicated circuitry where required
c) Gas outlets (natural)
d) Heating and cooling systems for each specific work area to avoid contamination

The following services are provided in specific areas of the laboratory:

a) Compressed air
b) Vacuum sources
c) Fume hoods
d) Dedicated electrical circuits

Instrumentation used is of the proper type and specification to perform routine and specialized analyses required by our clients. Standardized weights, certified thermometers, standard reference materials, calibration solutions, and electrical checks are used to assure proper instrumentation operation. Required service and cleaning procedures are on a scheduled basis. Service contracts are maintained on some of the instrumentation.

List of Major Capital Equipment

Teledyne-Tekmar Fusion TOC Analyzer (1)
Perkin Elmer 3300DV ICP Analyzer (1)
Perkin Elmer 3100 Flame Spectrophotometer (1)
Perkin Elmer 4100ZI Furnace Spectrophotometer (1)
Perkin Elmer Elan 9000 ICP/MS Analyzer (1)
Hewlett Packard 5890 GC (11)
Hewlett Packard 5972 MS (1)
Hewlett Packard 5973 MS (1)
Hewlett Packard 5971 MS (1)
Hewlett Packard 6890 GC (2)
Agilent 1100 HPLC (1)
Thermo Spectronic Genesys8 Visible Spectrophotometer (1)

Page 10

List of Major Capital Equipment, continued

Hach 2100N Turbidity Meter (1)
Milton Roy Spectronic 501 Visible Spectrophotometer (1)
Fisher Accumet AB30 Conductivity Meter
OI Flow Solution III (1)
OI Flow Solution IV (1)
Horizon Technologies SPE Oil & Grease Extraction

General laboratory equipment and supplies are of the proper type, materials, unique construction, and accuracy in calibration. All pipettes and glassware used for making standards are of the Volumetric Class A variety. Reagents and solutions purchased from outside vendors are labeled with the receiving date and the date opened. Shelf life recommendations and storage requirements are adhered to.

Reagents and solutions made in-house are labeled with the date made and an expiration date. A log book is kept with the date the solutions and reagents are prepared, the preparer's initials, and the exact quantities of chemicals used. The degree of purity of reagents, solvents, and gasses is dependent on what is being measured, the sensitivity of the method, and specificity of the detection system.

Cleaning procedures are based on the composition of the material, materials to be removed, and avoidance of introducing contaminants. A written cleaning program exists to insure standardized, consistent, and mandatory cleaning of all glassware and sample containers. Special cleaning required for some glassware may be found in specific method SOPs.

Page 11

Personnel Training

Environment 1 makes every effort to secure personnel who have extensive training or backgrounds in their job classifications. Even so, all new personnel are trained directly by another analyst in the following fashion:

a) Techniques are demonstrated by veteran staff with the veteran staff performing all the work until he/she feels confident the new employee can assist properly.
b) The new employee performs tasks under the direct supervision of veteran staff.
c) The new employee performs tasks alone, but reports to his/her supervisor before reporting data.
d) The new employee now performs their duties and submits his/her data with no supervisory inspection (it should be noted that at this point all final data is reviewed by the laboratory supervisor)

It is the policy of Environment 1 to adhere to the above training schedule no matter what the background of the new employee. While the new employee may have performed the same functions at his/her previous place of employment, procedures may vary and it is important to insure proper training in the techniques established by Environment 1 and as set forth in the Standard Operating Procedures Manual. An Analyst training log is maintained by management.

Page 12

Data Handling & Reporting

Environment 1 maintains a program for systematic and uniform recording of data, and for processing and reporting the data in the proper form for interpretation and use. Differing State and Federal programs require various reporting units and reporting formats. Clients are given specific ID numbers (refer to page 5, Sample Tracking in the Laboratory) which direct the data to be reported properly. Listed below are the important features of our data management system.

a) All samples have a client name, ID number, date received, and location code. This information, along with either a numerical result or specific data generated to enable the computer to calculate a numerical result, is supplied to data entry personnel. Calculations performed by the analysts are done using formulas reduced to simplest factors for quick, correct calculations. Significant figures are established for each analysis and rounding off rules is uniformly applied.

b) Control charts with control limits and warning limits are statistically calculated and recorded for most parameters. The entire "paper process" is kept to a minimum to avoid copying errors. Mechanisms exist to resolve data conflicts before final reporting of data.

c) Copies of lab reports, raw data, and quality control logs are kept for a length of time consistent with the regulatory requirements of particular programs and are either stored at the lab or at a secure off-site storage facility. Lab reports are kept for a minimum of 5 years for wastewater data and a minimum of 10 years for drinking water data.

d) To assure record integrity, lab results can only be amended or corrected by either the lab manager or lab supervisor. The original report is to be kept with the corrected report, and the corrected report is to have a notation that it is a corrected report.

e) Raw data reports are arranged in files by the month of analysis. In each monthly file cabinet analytical raw data is filed by method type and in chronological order by date of analysis.

f) Analytical result sheets are filed in alphabetical order by client name. Current year's result sheets along with the previous year's result sheets are Maintained on-site.

Analytical Quality Control

Quality Control can be defined as: those quality assurance actions which provide a means to control and measure the characteristics of measurements and processes to meet established requirements. Quality data consists of precision, accuracy, representativeness, comparability, sensitivity, and defensibility. The basic program incorporates the concepts calibration to attain accuracy, replication to establish precision limits, and correlation of quantitatively related tests to confirm accuracy. Overall effectiveness of a quality control program is not only dependent upon accuracy and precision but is also dependent upon the proper evaluation of equipment and instruments; the current state of the art; expected ranges of analytical results; the precision of the analytical method itself; control charts; and quality control results on a short-term (daily) basis as well as on an accumulated basis.

Precision, or the reproducibility of measurements under a given set of conditions, is attained using sample duplicates for all analytical parameters measured at Environment 1. EPA and other quality control samples are also analyzed in duplicate on some analyses. The determination of accuracy, which is the agreement of a

measurement to its true value or accepted reference value, is attained through the use of EPA and other quality control samples. While in house prepared standards may be used to develop curves, all analyses use second party knowns with each analytical run when available. Samples are spiked where practical or when called for by a specific method as not only another means of accuracy determination but also as a means to identify matrix interference problems.

Representativeness is achieved by the proper collection, handling and aliquoting of samples before and during analysis. Sample collection by Environment 1 is performed according to regulatory guidelines. Approved preservation and container requirements for all the various program protocols are adhered to. Care is taken to make sure the sample received in the laboratory is handled to insure representative data is generated.

Quality Control logs are maintained for individual parameters to provide comparability. These logs, along with standardized testing procedures insure day in and day out production of comparable data which is extremely important in compliance analyses.

Sensitivity requirements will vary with the many different environmental monitoring programs. Environment 1 maintains equipment and procedures to meet the sensitivity requirements for all the programs for which we maintain certification. Sensitivity is determined by detection level studies, program requirements, and matrix interferences. It should be understood that Method Detection Limits and Practical Quantitation Levels are not always the same. This fact underlines the necessity to identify analytical procedure /matrix problems in order to achieve the lowest possible PQL.

Page 15

Analytical Quality Control, (continued)

It is the goal of Environment 1 to generate data which is defensible by established Quality Control procedures. It is understood that defensibility must be achieved from sample collection to the final reporting of data.

Intra-laboratory Quality Control Program

The attainment and maintenance of this program is the direct responsibility of the Quality Control Coordinators. The intralaboratory program is divided into two areas: a routine program applicable to all test procedures and custom internal Quality Control programs for specific individual contracts.

Routine Intra-laboratory QC Program

1) Deionized water is monitored by both a continuous on-line monitor and also by grab sampling to assure that ASTM Type II grade reagent water is available for all analytical procedures.

2) Reference standards are NBS, EPA or certified to meet EPA standards. Expiration dates, when applicable, are included on standard solution labels.

3) Wavelength standard curves are rechecked with fresh standards with each use.

4) Analytical balances are checked against a 100 mg reference weight (ASTM Type 1, Class 1 or 2) each day of use. Balances are checked with a full range of Class S and/or Type 1 standards on a quarterly basis. Weights are re-certified Every 5 years or more often if there is reason to believe it is needed.

5) Deionized water blanks are analyzed with all chemistries when applicable.

Page 16

Analytical Quality Control, (continued)

6) All laboratory reagents meet ACS standards and are labeled indicating contents, date of preparation, analyst, and expiration date when applicable.

7) Only NBS Class A volumetric glassware is used in the preparation of standards.

8) Chemicals are dated upon receipt of shipment, dated when opened, and replaced as needed or before shelf life has expired.

9) Current service contracts and/or routine in-house maintenance and calibration programs are in effect on balances, visible spectrophotometers, atomic absorption spectrophotometers, gas chromatographs, GCMS, ICP, TOC analyzer, nutrient auto-analyzers, conductivity and pH meters, incubators, turbidity meters, and water purification system.

10) Records and files are maintained and available for easy reference or inspection. Hard copies of raw data and reports are kept for 3 years. Computer copies of reports are kept for 10 years.

11) All quality control logs and data are maintained and available for easy reference or inspection.

12) All Analytical reports can be signed by John Melvin and Steve Jones. Ann Brown may sign all drinking water analytical reports and Rebecca Lomas may sign drinking water BACTI analytical results.

13) Analytical reports can be changed by John Melvin and Steve Jones.

14) Quality control data is not routinely supplied with analytical reports unless specifically requested by the client.

Page 17

Custom Quality Control Programs

In addition to the routine intra-laboratory QC program, custom QC programs can be designed for individual contract efforts. Programs can be tailored to the individual client's needs including:

a) Chain of Custody documentation
b) Modified sample holding times
c) Sample compositing
d) Modified analytical procedures
e) Experimental studies

It is understood that any variations from established and required QC protocols will exempt the data from being used for compliance reporting to governmental agencies. A notation on the final report for data not adhering to proper QC protocols will be included.

Page 18

Safety Considerations

While safety rarely has a direct effect on quality laboratory data production, it still must be included in the overall laboratory quality assurance program. A written safety program and Chemical Hygiene Plan as required by OSHA, specific for laboratories, exists and a copy is located in each employee handbook. Regularly scheduled safety meetings are held and employee attendance and participation are required. Employees are required to read the **HAZARD COMMUINCATION PROGRAM** and the **CHEMICAL HYGIENE PLAN** found in the employee handbook. Any questions should be directed to the Safety Officer.

The laboratory facility is designed and maintained to insure a safe working environment exists. All wiring, plumbing, and ventilation has been installed, and when repairs are necessary performed, in compliance with pertinent building codes. Analytical equipment and related appurtenances are maintained in safe and proper working order.

Emergency equipment such as fire extinguishers, spill clean-up kits, eyewash stations, body showers, burn stations, first aid kits, and fume hoods are provided at key locations in the laboratory. Personal safety equipment such as lab coats, face shields, gloves, safety glasses, and respirators are provided to each analyst as needed. **Each employee is instructed to use all necessary safety equipment needed for each particular task undertaken.** Material Safety Data Sheets are maintained in alphabetical order and available to all employees. If you have safety concern issues or feel you need additional safety protection for your particular job bring it to the attention of the Safety Officer.

Personal safety as specified in the **CHEMICAL HYGIENE PLAN** must be adhered to. Violations will be handled as follows. The first offense will result in a verbal warning. The second offense will result in a written warning. The third offense will result in loss of a day's wages.

Page 19

Summary

The ability to maintain a high level of quality assurance requires planning, control, and checking for every phase of operation from sample collection through the storage of data. An effective program requires that procedures are written, responsibilities are clearly defined and assigned, and individuals and procedures held accountable. Environment 1 maintains the above quality assurance measures to insure the data reported is valid and representative of the matrix analyzed.

This document shall be reviewed on an annual frequency or sooner if needed. The review process shall be conducted by John Melvin and Steve Jones and shall include all aspects of the document. This document can be changed only by either John Melvin or Steve Jones.

Appendix 6
to the UNRBA Monitoring Program QAPP

Standard Operating Procedures
Environment 1, Inc.

Table of Contents

Sample Collection for River Basin Coalitions

Revision date: 07/08/14

"Monitoring Coalition Program Field Monitoring Guidance V2.0 Dec. 2012" from NCDWR-ESS Ecosystems Unit provides extensive background on this type of sample collection.

Sampling Supply List:

Cooler(s) of labeled sample bottles with COC forms
Bridge sampler with rope (and pole if needed)
Bailer/Transfer bottles
Meter Calibration cooler (DI water, conductivity stds., pH buffers…)
YSI 556MPS Meter (bring backup meter if available)
Cooler(s) of ice
Dashboard GPS unit (with sampling locations saved internally)
Calibration sheet, DO table, Field notepad, binder with Field Sampling Forms
Reflective safety vest

1. Calibrate the YSI 556MPS meter per "Calibration Instructions" and replace the calibration cup with the weighted sampling guard.

2. Park in a safe location off the roadway. Insert the bailer/transfer bottle and the sterile Fecal Coliform bottle into the sampler. Put on safety vest.

3. Sample collection should be done from the upstream side of the bridge whenever possible. If the downstream side is used, document that on the Field Sampling Form along with the explanation (traffic pattern/ safety, logs/debris piled up on bridge supports…)

4. Grab sample:

    a. Lower the meter cable so that the probe is just completely submerged. Do not allow the probe impact the stream bed. Set the handheld unit and backpack aside allowing time for the meter readings to settle.
    b. Remove the caps from both bottles and store in a zip lock bag. Lower the sampler into the main stream channel whenever possible. The mouths of the bottles should be just under the surface of the water(approximately 0.1 meter).
        i. Pull the rope or pole up slowly when the bottles are full.
        ii. Use care not to drag the rope or bounce the sampler on the bridge.
        iii. Cap both bottles. Replace the bailer/transfer bottle with another if additional sample volume is needed.

Prepared by: _____

c. Record the sample collection date, time and field parameters in the notebook. Also record precipitation and stream flow rating using the Field Sampling form. Record any other observations in the comments section.
d. Coil the meter cable and store in the backpack. Use caution as the probe approaches the bridge as it can be damaged with impact.
e. Pour off other sample bottles from the bailer/transfer bottle as needed. Seal the sample bottles in zip lock bags and store on ice immediately.

5. Field Filtering (if required)

a. Carry the following supplies: Millipore 0.45 um membrane filters(47mm), glass fiber filters, Pall Gellman magnetic filter funnel, suction flask, latex or nitrile gloves
b. Rinse the entire filet apparatus with approximately 200ml of DI water and discard the filtrate. Filter sufficient sample volume (approx. 200ml per nutrient bottle) through a glass fiber filter.
c. Discard the GFF and replace with a Millipore membrane filter. Run the GFF filtrate through the membrane and pour into the client labeled soluble nutrient bottle. Multiple membrane filters may be needed if the filter becomes blocked.

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P.O. Box 7085, 114 Oakmont Dr.
Greenville, NC 27858
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Phone (252) 756-6208 • Fax (252) 756-0633

CHAIN OF CUSTODY RECORD

CLIENT: 1103 **Week:** 29

DISINFECTION
☐ CHLORINE
☐ UV
☐ NONE
☐ _____

SAMPLE LOCATION	COLLECTION DATE	COLLECTION TIME	TOTAL CHLORINE, mg/l OR ug/l AT COLLECTION	TEMPERATURE, °C AT COLLECTION	# OF CONTAINERS	Field pH	Fecal Coliform	TSR	Ammonia Nitro.	TKN	Nitrate-Nitrite	T. Phosphorus	Turbidity	DO	Conductivity	Temperature	Field Parameter	CLA			
CHLORINE NEUTRALIZED AT COLLECTION																					
pH CHECK (LAB)																					
CONTAINER TYPE, P/G						P	P	P	P	P	P	P	P	P	P	P		P			
CHEMICAL PRESERVATION						A	G	A	C	C	C	C	A	A	A	A		A			
Station 24					6																
Station 25					6																
Station 26					6																
Station 27					6																
Station 28					6																
Station 29					6																
Station 41					7																
Station 42					7																
Station 45					7																

PARAMETERS/TESTS

A - NONE D - NAOH
B - HNO_3 E - HCL
C - H_2SO_4 F - ZINC ACETATE/NAOH
G - NA THIOSULFATE

CLASSIFICATION:
☐ WASTEWATER (NPDES)
☐ DRINKING WATER
☐ DWQ/GW
☐ SOLID WASTE SECTION

CHAIN OF CUSTODY MAINTAINED DURING SHIPMENT/DELIVERY
Y N

SAMPLES COLLECTED BY:
(Please Print)

SAMPLES RECEIVED IN LAB AT _____ °C

RELINQUISHED BY (SIG.) (SAMPLER)	DATE/TIME	RECEIVED BY (SIG.)	DATE/TIME
RELINQUISHED BY (SIG.)	DATE/TIME	RECEIVED BY (SIG.)	DATE/TIME
RELINQUISHED BY (SIG.)	DATE/TIME	RECEIVED BY (SIG.)	DATE/TIME

COMMENTS:

PLEASE READ Instructions for completing this form on the reverse side.

FORM #5

Sampler must place a "C" for composite sample or a "G" for Grab sample in the blocks above for each parameter requested.

№ 277982

Revision Date: 07/08/14

pH Determination using YSI 556MPS meter for River Basin Coalitions
Standard Methods 4500H-B-2000

(This procedure can be found on page 4-90 in "Standard Methods for the Analysis of Water and Wastewater", 21st Edition)

Before you begin make sure you have the following:

YSI 556 MPS meter, spare set of 4 "C" batteries, screwdriver
DI water for rinsing the probe and calibration cup
The following Ricca pH buffers or equivalent:

1501-16	pH 4.00 buffer
1551-16	pH 7.00 buffer
1601-16	pH 10.00 buffer

1) Follow the calibration procedure outlined in "YSI 556 Calibration Instructions". There must be a "mid-day" calibration check after a maximum of six hours of use and an "end of day" at the completion of use for that day.

2) All measurements are taken in-stream per "MONITORING COALITION PROGRAM FIELD MONITORING GUIDANCE, V 2.0 Dec. 2012" from NCDWR-ESS Ecosystems Unit. Record the pH reading in the field notebook when both the temperature and pH values have settled. For final reporting purposes, pH readings are reported to the nearest .1 SU.

3. Since the YSI 556 MPS meter is an Automatic Temperature Compensation unit, no calculations are necessary.

Quality Control

-All calibration checks (initial, mid-day & end of day) must meet +/- 0.1 SU of the buffer true value at the current temperature. Any sample readings that are not bracketed by acceptable calibration checks will be flagged with a J12 remark code.

-If the meter will not calibrate (out of range) or fails a calibration check, probe cleaning or other maintenance may be required.

Prepared by: Mark Oliveira

Page 1 of 1

Revision Date: 07/08/14

CONDUCTIVITY using YSI 556MPS meter for River Basin Coalitions

STANDARD METHODS 2510B-1997

(This procedure can be found on page 2-46 in "Standard Methods for the Examination of Water and Wastewater", 21st Edition)

Before you begin make sure you have the following:

YSI 556 MPS meter, spare set of 4 "C" batteries, screwdriver
DI water for rinsing the probe and calibration cup
Ricca Potassium Chloride conductivity standards or equivalent:

5886.5-32	50	uS/cm KCl
5888.01-32	1000	uS/cm KCl
5888.20-32	20,000	uS/cm KCl

1) Follow the calibration procedure outlined in "YSI 556 Calibration Instructions". There must be a "mid-day" calibration check after a maximum of six hours of use and an "end of day" calibration check at the completion of use for that day. The 20,000 us/cm standard is only analyzed if a stream reading exceeds 1000 us/cm.

2) All measurements are taken in-stream per "MONITORING COALITION PROGRAM FIELD MONITORING GUIDANCE, V 2.0 Dec. 2012" from NCDWR-ESS Ecosystems Unit. Record the Specific Conductance reading (us/cm) in the field notebook when both the temperature and Specific Conductance readings have settled.

3) Since the YSI 556 MPS meter is an Automatic Temperature Compensation unit, no calculations are necessary.

Quality Control

-All calibration checks (initial, mid-day & end of day) must meet +/- 10% of the standard true value. Any sample readings that are not bracketed by acceptable calibration checks will be flagged with a J12 remark code.

-If the meter will not calibrate (out of range) or fails a calibration check, probe cleaning or other maintenance may be required.

-The ATC function of the meter must be checked annually. If the meter does not meet the ATC check criteria, the test can be repeated, or maintenance may be required.

Prepared by:  Page 1 of 1
Mark Oliveira

Conductivity, Page 1 of 1

1

Revision Date: 07/08/14

Dissolved Oxygen - Membrane Electrode Method for River Basin Coalitions Standard Methods 4500-OG-2001.

(This procedure can be found on page 4-141 in "Standard Methods for the Analysis of Water and Wastewater", 21st Edition)

1) Follow the calibration procedure outlined in "YSI 556 Calibration Instructions". There must be a "mid-day" calibration check and recalibration after a maximum of six hours of use. Also, an "end of day" calibration check must be done at the completion of use for that day.

2) All measurements are taken in-stream per "MONITORING COALITION PROGRAM FIELD MONITORING GUIDANCE, V 2.0, Dec. 2012" from NCDWR-ESS Ecosystems Unit. Record the Dissolved Oxygen reading (mg/L) in the field notebook when both the temperature and D.O. readings have settled.

3) Since the YSI 556 MPS meter is an Automatic Temperature Compensation unit, no calculations are necessary.

Quality Control

-All calibration checks (initial, mid-day & end of day) must meet +/- 0.5 mg/L of the D.O. table value for the current location and temperature. Any sample readings that are not bracketed by acceptable calibration checks will be flagged with a J12 remark code.

-If the meter will not calibrate (out of range) or fails a calibration check, probe cleaning, membrane/electrolyte replacement or other maintenance may be required.

-The temperature probe of the meter must be checked annually against a NIST thermometer. If the temperature does not read within +/- 1.0 C, the meter will need to be sent to YSI for service.

Prepared by: M A. Ce
Mark Oliveira

Page 1 of 1

Upper Neuse Basin Association

Field Sampling Form

HUC	Station	Sample Location	County
XXXXXXXX	**LL04**	**Eno River at Old Oxford Highway**	**Durham**

Client ID/#: 1400

Location Code: LL04

Parameter	Instantaneous In-Stream Measurement Time	Results
Dissolved Oxygen, mg/l		
Temperature, °C		
pH, S.U.		
Conductivity, uS/cm		

Precipitation (circle one): 0 (none) 1 (light rain) 2 (steady/heavy rain) 3(snow)

Stream Flow(circle one): 0 (no visible flow) 1 (low) 2 (average) 3 (high)

Collection Date: _____

Analyst Initials: _____

Comments:

_____

_____

_____

_____

1

YSI 556 MPS Calibration Instructions

Revision Date: 11/11/11

Initial (daily) Calibration:

Record the Date, Analyst initials and meter serial number at the top of the Calibration Log Sheet. Record all pH buffer and Conductivity Std. consumable information on the back side of the Calibration Log Sheet.

Conductivity Calibration

1. Power on the meter.

2. Rinse the probes and calibration cup using a squirt bottle filled with DI water.

3. Rinse the probes and calibration cup with the 1000 Us/cm standard. Fill the cal. Cup approximately ¼ full, replace the cup and shake. Discard the rinse.

4. Fill the cup with 1000 Us/cm standard until it covers the side hole on the conductivity probe.

5. Press "Esc." to go to the main menu.

6. Scroll to "calibrate" and press enter.

7. Scroll to "conductivity" and press enter.

8. Scroll to "specific conductance" and press enter.

9. Enter the calibration value "1.000 ms/cm" if it is not already displayed and press enter.

10. After the conductivity reading settles, and while the display says "calibrate" at the top, record the "before calibration" conductivity reading on the cal. Sheet.

11. Press enter and the "calibrate" at the top of the screen will change to "continue". Also, the conductivity reading will change to "1000". Record the time on the cal. sheet.

12. Press enter while "continue" is at the top of the display.

13. Press escape 3 times to get to the Run Menu.

14. Repeat steps 2 thru 4 using the 50 Us/cm standard and record the meter reading on the cal. Sheet when it has settled.

15. Press escape to the Main Menu.

Conductivity Calibration (continued)

16. Scroll to "File" and press enter.

17. Scroll to "directory" and press enter.

18. Scroll to "filename" and press enter.

19. Scroll to "view file" and press enter.

20. Scroll to today's date and press the right arrow. Record the Conductivity Gain value (x.xxx) as the cell constant on the cal. Sheet.

pH Calibration

1. Escape to the Run Menu.

2. Rinse cup and probes with DI water.

3. Rinse cup and probes with 7.00 buffer (cup approx. ¼ full)

4. Fill cup approx. 1/3 full with 7.00 buffer and replace.

5. Allow temp. and pH readings to settle.

6. Record buffer temp. and "pre-cal." Reading on the cal. Sheet.

7. Escape to Main Menu.

8. Scroll to "calibrate" and press enter.

9. Scroll to "pH" and press enter.

10. Scroll to "3 point" and press enter.

11. Using the table on the side of the buffer bottle, enter the "temperature corrected value" (i.e. if the 7.00 buffer is 20 deg. C, enter "7.02") and press Enter. Record this value on the sheet.

12. Press enter and record the "calibrated value" on the sheet. Also record the time.
*(**Do not press enter while "continue" is displayed at the top of the screen**)*

pH Calibration (continued)

13. Repeat steps 2 thru 6 with the 4.00 buffer, then continue with step 14.

14. Press enter while "continue" is displayed at the top of the screen and repeat steps 11 and 12 for the 4.00 buffer.

15. Repeat steps 13 and 14 for the 10.00 buffer.

16. Press enter to continue. Escape to the Run Menu.

17. Repeat steps 2 thru 5 with the 7.00 buffer and record the temperature, Temperature corrected value, and pH reading.

Dissolved Oxygen Calibration

******D.O. must be calibrated on-site at the 1st sampling station******

1. Rinse probes and cup with DI water.

2. Dry DO membrane and temperature sensor with Kimwipe.

3. Add approx. 1/8" DI water to the calibration cup and thread it **loosely** onto the cable end. Make sure the calibration cup remains in the vertical position so that the water will not touch the temp. sensor or DO membrane.

4. Allow the temp. and DO readings to settle(approx. 10-15 min.), and record the Temp. D.O. % and D.O. mg/l in the "before cal." section of the sheet.

5. Escape to Main Menu.

6. Scroll to "calibrate" and press enter.

7. Scroll to "D.O. 2 mil PE Blue" and press enter. (if not blue, configuration is wrong!)

8. Scroll to "D.O. %" and press enter.

9. Record the Barometric Pressure setting that was already entered.

10. Enter the B.P. for your current location and press enter (record on the sheet).

Dissolved Oxygen Calibration(continued)

11. Press enter when "calibrate" is displayed at the top of the screen. Record the temperature, D.O. % and D.O. mg/l on the cal. sheet.

12. Press enter when "continue" is displayed at the top of the screen.

13. Escape to the Run Menu.

14. Use the Dissolved Oxygen Table to find the theoretical D.O. (mg/l) for the current temperature and barometric pressure. Record this on the sheet.

Mid-day Calibration (recommended)

1. Read the 1000 uS/cm conductivity standard and record on cal. sheet. Recal. if needed.

2. Read the ph 7.00 and 4.00 buffers using their temperature corrected values. Recal. if needed.

3. Recalibrate the D.O. as described in the previous section.

End of day Calibration (required)

1. Read 1000 Us/cm conductivity standard and record on cal. sheet. Recal. if needed.

2. Read the ph 7.00 and 4.00 buffers using their temperature corrected values. Recal. if needed.

3. Perform steps 1 thru 4 of the D.O. calibration section and record the readings. The meter does not need to be recalibrated at this point.

Prepared by: _____
Mark Oliveira

1

CALIBRATION LOG SHEET

Meter: YSI 556MPS

Date: _____ **Analyst Initials** _____ **S.N.:**_____

Dissolved Oxygen Initial Calibration Time: _____	**Before Initial Calibration**	**After Initial Calibration**
B. P. Setting (mmHg)		
Temp. Reading (deg. C)		
D. O. Reading (% Sat.)		
D.O. Reading (mg/L)		
	+/- 0.5 mg/L of Table value	(Y) (N)
	Table value for current location (mg/L)	

Conductivity Initial Calibration	**Confirmation Standards**	**Results**	**Acceptance Limits (±10%)**
(1000 umho/cm Std.)	20,000*		(18,000-22,000)
Pre-cal reading:	50 umho/cm		(45-55)
Time: _____	Cell Constant		(0.8-1.2)

*Used only when field readings above 1000 umho/cm are observed.

pH Initial Calibration Time:_____	**pH 7.0 Buffer**	**pH 4.0 Buffer**	**pH 10.0 Buffer**	**pH 7.0 Buffer Verification**
Buffer Temp. (deg C)				
Temp. corrected value				
Pre-calibration reading				
Post-calibration reading				
+/- 0.1 SU				(Y) (N)

==========

Dissolved Oxygen Mid-day Calibration Time: _____	**Before Mid-day Calibration**	**After Mid-Day Calibration**
B. P. Setting (mmHg)		
Temperature Reading (deg. C)		
D. O. Reading (% Sat.)		
D.O. Reading (mg/L)		
+/- 0.5 mg/L of Table value	(Y) (N)	(Y) (N)
Table value for current location(mg/L)		

Conductivity Mid-Day Calibration Check	**Confirmation Standard**	**Results**	**Recalibration**
Time:	1000 umho/cm		
		= ± 10% (900-1100)? (Y) (N)	Recalibrated? (Y) (N)

2

CLS for YSI556MPS Date:_____ Analyst:_____ S.N.:_____

pH Mid-Day Cal. Check (7.0)	pH 7.0 SU Reading	+/- 0.1 SU	pH 4.0 SU Reading	+/- 0.1 SU	Recalibrated ?
Time:		(Y) (N)		(Y) (N)	(Y) (N)
Temp:					
Temp. corrected value					

==========

Dissolved Oxygen End of day Calibration check Time: _____	End of Day Calibration Check
B. P. Setting (mmHg)	
Temperature Reading (deg. C)	
D. O. Reading (% Sat.)	
D.O. Reading (mg/L)	
+/- 0.5 mg/L of Table value	(Y) (N)
Table value for current location (mg/L)	

Conductivity End of Day Calibration Check	Confirmation Standard	Results
Time:	1000 umho/cm	
		= ± 10% (900-1100)? (Y) (N)

pH End of Day Calibration Check	pH 7.0 SU Reading	+/- 0.1 SU	pH 4.0 SU Reading	+/- 0.1 SU
Time:		(Y) (N)		(Y) (N)
Temp.				
Temp. corrected value				

Description	Ricca Cat. #	Lot #	Date Received	Date Opened	Exp. Date
pH 4.00 buffer	1501-16				
pH 7.00 buffer	1551-16				
pH 10.00 buffer	1601-16				
50 uS/cm Cond.	5886.5-32				
1000 uS/cm Cond.	5888.01-32				
20K uS/cm Cond.*	5888.20-32				
PH 2 standard**	PH-2-5				

*Used only if conductivity readings greater than 1000 umho/cm are observed.
** Used only if pH readings less than 4.0 observed.
Revision Date: 07/03/14

Revision/Review Date: 11/04/13

AMMONIA NITROGEN (PERSTORP)
EPA METHOD 350.1 Revision 2.0 (1993)

(This method can be found on page 350.1 in the EPA manual, "Methods for Chemical Analysis of Water and Wastes", March 1983)

TEMPERATURE - 50C GAS - NITROGEN

REAGENTS ---- NITROPRUSSIDE, HYPOCHLORITE, ALKALINE PHENOL, EDTA
START-UP SOLUTION (BRIJ 2ML/L)

1) Turn on **analyzer first** then computer. Connect pump tubes according to flow diagram. Make sure heater is set to 50 oC.

2) Place sampler wash line in 0.3% sulfuric acid. Pump start-up solution through system. Adjust pump tensions so you get a good chemical and air flow. Connect pump tubes to reagents.

3) In WINDOWS select the "WINFLOW" icon.

4) Select MNH3 sample table and method table, and enter a file name for this run.

5) Load sample trays according to data sheets and computer sample table. Standards are 0.01(or 0.04), 0.50, 2.00, 4.00, and 8.00 mg/l. A 2nd source must be analyzed with each run supplied by either a different vendor or a different lot number from the curve standards. Spikes are to be prepared using a different vendor or lot number from the curve standards as well.

6) Select "run" from the tool bar.

7) When run is complete check peak markers and standards, adjust if necessary.

8) Print curve, statistics, and sample report.

Reagents:

Alkaline Phenol. (Prepare under a fume hood wearing gloves.) In a 500 ml. flask with approx. 350 mls. DI water add while stirring 40 mls. of 10N NAOH. Add 47 mls. of liquefied phenol. Dilute to 500 mls. with DI water. Store in amber bottle and refrigerate. **Make fresh every 15 days.**

Hypochlorite Solution. Dilute 85.5 mls. of bleach to 200 with DI water in a volumetric flask. **Prepare fresh each day.**

Nitroprusside Solution. In a 1 L volumetric flask add approximately 700 mls. of DI water. Add 0.5 g sodium nitroprusside and mix. Dilute to mark. Store in amber bottle at room temperature. **Make fresh every 10 days.**

Prepared by: Steve Jones

Page 1 of 2

Ammonia Nitrogen, Page 2 of 2

Stock EDTA Solution. In a 1.5 L beaker add approx. 900 mls. of DI water. Add 5 grams disodium EDTA and mix. Adjust pH to 9.0 +-0.1 with 50 % NaOH. Pour into 1 liter volumetric flask and dilute to mark. **Make fresh every 10 days.**

Working EDTA Solution. Add 5 drops of Brij to every 100 mls of stock EDTA used for the day's run.

10N NAOH. In a 1 liter volumetric flask add 600 mls. of 50% liquid NAOH. Dilute to mark with DI water and mix. After cooling top off to mark.

Stock Standard. In a 1 L volumetric flask add approx. 800 mls. DI water and 1 ml. chloroform. Add 2.3585g of dried ammonium sulfate and mix. Add 6 mls. 50% H2SO4 and dilute to mark. **NH3 = 500 mg/l**

Intermediate Standard. In a 250 ml. volumetric flask add 10.00 mls. stock. Dilute to mark with DI water & mix. **NH3 = 20 mg/l**

Working standards. ml. of inter. standard	mg/l N
*(0.5 ml. of 2.0 std.)	0.01
*(2.0 ml. of 2.0 std.)	0.04
2.5	0.50
10.0	2.00
20.0	4.00
40.0	8.00

* Make depending on which reporting level you are using.

Add the above amounts of intermediate standard **(using volumetric flasks)** to 100 ml. volumetric flasks.

Quality Control
-Analyze duplicate every 20 samples. (see QC guidelines)
-Analyze 2nd Source Std. daily. (±15% recovery or 95% CI)
-Analyze 4.00 mid-point std. at the beginning of each run, at the end of each run and every 10 samples. (Must be +-10% recovery)
-Analyze a spike for every 20 samples (±20% recovery)
-Only use curve points that are +-10% except for the 0.04 which may be +-25%. (0.02 - 0.06)
-8.0 std. must be +-10% recovery to proceed.
-Holding time is 28 days at 4C.
-Analyze a blank daily.

Revision/Review Date: 11/04/13

NITRATE-NITRITE (PERSTORP)
EPA METHOD 353.2 Revision 2.0 (1993)

(This method can be found on page 353.2 in the EPA manual, "Methods for Chemical Analysis of Water and Wastes", Aug 1993 revision 2.0)

TEMPERATURE - NONE GAS - NITROGEN

REAGENTS ---- BUFFER, COLOR REAGENT, DI WATER

1) Turn on **analyzer first** then computer. Connect pump tubes according to flow diagram and bubble line to Nitrogen supply.

2) Place sampler wash line in DI water. Pump Brij solution through 2 reagent lines. Adjust pump tensions so you get a good chemical and air flow. **CHECK pH OF BUFFER BEFORE YOU CONNECT PUMP TUBES TO REAGENTS.** After buffer in system connect Cadmium coil.

3) In WINDOWS select the "WINFLOW" icon.

4) Select MNO3 sample table and method table, and enter a file name for this run.

5 Load sample trays according to data sheets and computer sample table. Neutralize samples to a pH of between 5 and 9 with Ammonium Hydroxide. Check for chlorine and neutralize with sodium thiosulfate if necessary. The curve shall consist of a blank and standards: 0.04, 0.50, 2.00, 4.00, and 8.00 mg/l. **Some client specific requirements require a low standard of 0.01 mg/l.** On days where the 0.01 low standard is required, it is used in place of the 0.04 mg/l standard in the curve. Pour a fresh 2.00 mg/l NO2 standard and place it in the proper cup for column efficiency check. A 2nd source must be analyzed with each run supplied by a different vendor from the curve standards. Spikes are to be prepared using a different vendor from the curve standards as well.

6) Select "run" from the tool bar.

7) Print curve, statistics, and sample report.

Reagents:

Buffer Solution. In a 1 liter **beaker** add approx. 700 mls. DI water. Add 85 grams Ammonium Chloride and 0.1 grams of Disodium EDTA. Adjust pH of buffer with Ammonium Hydroxide so that the pH of the sample reaching the Cadmium Coil is **8.8.** Pour in a 1 liter volumetric flask and fill to volume with DI water. Add 1 ml of Brij. **Check pH each day before using, adjust if necessary. Good for 1 month.**

Color Reagent. In a 1 liter volumetric flask add approx. 600 mls. of DI water. Add 100 mls. Conc. Phosphoric Acid. Add 40 grams of Sulfanilimide and 2 grams of N-1-naphthylenediamine dihydrochloride. Fill to mark with DI water. Store in amber bottle in the dark. **Good for 1 month.**

Prepared by: Steve Jones

Nitrate-Nitrite, Page 2 of 2

Stock Standard. Dry approx. 1 gram of Potassium Nitrate in an oven at 100-105 oC for 2 hours. Dessicate until cool for at least 2 hours. In a 1 liter volumetric flask add approx. 800 mls. of DI water. Add 0.7218 g Potassium Nitrate and mix. Add 6 mls. of 50% H_2SO_4 and 2 mls. of Chloroform. Dilute to mark. **100 mg/l**

Working standards.

ml. of stock standard	mg/l N
0.0	0.00
*(1 ml. of 1.0 std)	0.01
*(2 ml. of 2.0 std)	0.04
0.5	0.50
1.0	1.00
2.0	2.00
4.0	4.00
8.0	8.00

* Make depending on which reporting level you are using.
Add the above amounts of stock standard to 100 ml. volumetric flasks.

Quality Control
-Analyze a duplicate every 10 samples for drinking water (±10%) and every 20 samples for wastewater(see QC guidelines).
-Analyze a 2nd Source Std. daily. (±10% for drinking water and ± 15% for wastewater samples.
-Analyze a 4.0 std. after the calibration curve, every 10 samples and one at the end of the sample run. (Must be +-10% recovery)
-Curve must be 0.995 to proceed.
-Low curve standard must be ± 50%.
-8.0 std. must be +-10% recovery to proceed.
-Analyze a blank after every 10 samples and one at the end of the run.
-Holding time is 28 days at 4C, if NO_2 analyzed within 48 hours.
-Analyze a spike for every 10 drinking water samples (±10%R) and every 20 wastewater samples (±20%R)
-Neutralize residual chlorine if necessary with sodium thiosulfate.
-Adjust sample pH to between 5 & 9 units with ammonium hydroxide before analysis if needed.
-Determine MDL for each analyst every 6 months or more frequently as needed.

-Compute column efficiency:

$$\frac{NO_3 \text{ Standard}}{NO_2 \text{ Standard}} \times 100$$

Must be +-25%

Cadmium Coil Re-Generation. (as needed)
1) Flush with 10 mls. DI water. If debris is seen continue to flush.
2) Flush slowly with 10 mls. 0.5N Hydrochloric Acid. Proceed quickly to next step.
3) Flush with 10 mls. buffer containing no Brij.
4) Flush slowly with a 1:1 mixture of buffer containing no Brij and 2% Cupric Sulate. Perform this step slowly over 3 minutes. Push some through, step away, push more through, etc.
5) Flush forcefully with 10 ml. of buffer containing no Brij to remove any loose copper. Continue to flush until there is no more debris.
6) Fill the column with buffer containing no Brij for storage.

Revision/Review Date: 06/27/14

TOTAL KJELDAHL NITROGEN (PERSTORP)
EPA METHOD 351.2 Revision 2.0 (1993)

(This method can be found of page 351.2 of the EPA manual,
"Methods for Chemical Analysis of Water and Wastes" Revision 2.0 (August 1993)

TEMPERATURE -------- 37C GAS - NITROGEN

REAGENTS ----- SALICYLATE/NITROPRUSSIDE, HYPOCHLORITE, BUFFER,
START-UP SOLUTION (BRIJ 2ML/L), 4% H2SO4

1) Turn on **analyzer first** then computer. Connect pump tubes according to flow diagram. Make sure heater is set to 37 oC.

2) Place sampler wash line in 4% sulfuric acid. Pump start-up solution through system. Adjust pump tensions so you get a good chemical and air flow. Connect pump tubes to reagents CONNECT **SALICYLATE REAGENT 5 MINUTES AFTER THE OTHERS AND WHEN FINISHED DISCONNECT FIRST.**

3) In WINDOWS select the "WINFLOW" icon.

4) Select the MTKN sample and method tables, and enter a file name for this run.

5) Load sample trays according to data sheets and computer sample table. Standards are 0.20, 5.00, 10.00, and 20.00 mg/l. A 2nd source must be analyzed with each run supplied by either a different vendor or a different lot number from the curve standards. Spikes are to be prepared using a different vendor or lot number from the curve standards as well.

6) Select "run" from the tool bar.

7) When run is complete check peak markers and standards, adjust if necessary.

8) Print curve, statistics, and sample report.

Reagents:

Hypochlorite Solution. In a 200 ml. volumetric flask add 12 mls. of hypochlorite solution (5% Bleach). Fill to mark with DI water. **Make fresh daily.**

Salicylate/Nitroprusside Solution. In a 500 ml. volumetric flask add approximately 250 mls. of DI water. Add 150 grams Sodium Salicylate and 0.3 grams Nitroprusside and mix. Dilute to volume with DI water. Store in an amber bottle at room temperature. **Make fresh every 30 days**

10N Sodium Hydroxide. In a 1 liter volumetric flask add 600 mls. of 50% liquid NaOH. Dilute to volume with DI water. After cooling, top off to the 500 ml. mark with DI water.
Make fresh every 30 days

Prepared by: Steve Jones

TKN, Page 2 of 2

4% Sulfuric Acid Solution. Place approx. 500 mls. DI water in a 1 liter volumetric flask. Cautiously add 40 mls. Conc. Sulfuric Acid. Fill to volume with DI water.

Stock Buffer. In a 1 liter volumetric flask add approx. 600 mls. DI water. Add 135 grams of Sodium Phosphate Dibasic and 50 mls. of 10N Sodium Hydroxide and mix. Fill to volume with DI water and mix. **Make fresh every 30 days.**

Working buffer Solution. In a 500 ml. volumetric flask add approx. 300 mls. DI water and the following in order:

Stock Buffer	100 mls.
10N Sodium Hydroxide	30 mls.
Sodium Potassium Tartrate (50%)	5 mls.

Fill to volume with DI water and mix. Add 0.5 mls. Brij. **THIS SOLUTION MAY NEED TO BE FILTERED BEFORE ADDING BRIJ.** Make fresh every 14 days.

Working standards. See digestion procedure.

Quality Control
-Analyze a duplicate every 20 samples. (see QC guidelines)
-Analyze a 2nd Source Std. daily. (±15% recovery)
-Analyze a 10.0 std. at the beginning of each run, at the end of each run, and every 10 samples. (Must be ±10% recovery)
-Analyze a matrix spike for every 20 samples (±20 % recovery).
-Only use curve points that are ±10% except for the 0.20 which may be ±50%. (0.10 - 0.30)
-**20.0 std. must be ±10% recovery to proceed.**
-Analyze a blank daily.
-Holding time is 28 days at 4C.

2

Revision/Review Date: 11/04/13

TOTAL PHOSPHORUS (PERSTORP)
EPA METHOD 365.4 Revision 2.0 (1993)

(This method can be found on page 365.4 in the EPA manual,
"Methods for Chemical Analysis of Water and Wastes", March 1983)

Digestion Method: Block using Mecuric Oxide,Potassium Sulfate, H2SO4

TEMPERATURE ------- 37C GAS - NONE

REAGENTS ---- ASCORBIC ACID, MOLYBDATE/TARTRATE, DILUENT
4% H2SO4, START-UP SOLUTION (4% H2SO4)

1) Turn on **analyzer first** then computer. Connect pump tubes according to flow diagram. Make sure heater is set to 37 oC.

2) Place wash line in 4% sulfuric acid. Pump start-up solution through system. Adjust pump tensions so you get a good chemical and air flow. Connect pump tubes to reagents. **CONNECT MOLYBDATE/TARTRATE LINE 5 MINUTES AFTER THE OTHERS AND REMOVE FIRST WHEN THE RUN IS COMPLETE.**

3) In WINDOWS select the "WINFLOW" icon.

4) Select the MPO4 sample and method tables, and enter a file name for this run.

5) Load sample trays according to data sheets and computer sample table. Standards are 0.02, 0.40, 0.80, 4.00,and 8.00 mg/l. A 2nd source must be analyzed with each run supplied by either a different vendor or a different lot number from the curve standards. Spikes are to be prepared using a different vendor or lot number from the curve standards as well.

6) Select "run" from the tool bar.

7) When run is complete check peak markers and standards, adjust if necessary.

8) Print curve, statistics, and sample report.

Reagents:

4% H2SO4. Place approx. 500 mls. DI water in a 1 liter vol. flask. Cautiously add 40 mls. Conc. Sulfuric Acid. Fill to volume with DI water.

Diluent. In a 1 liter vol. flask add approx. 600 mls. DI water. Add 15 grams Sodium Chloride (NaCL) and mix. Fill to volume with Di water and mix. Add 2 mls. Dowfax.

Ascorbic Acid. In a 250 ml. vol. flask add approx. 150 mls. DI water. Add 15.0 grams Ascorbic Acid and mix. Fill to volume with DI water. **Make fresh every 10 days.**

Prepared by: Steve Jones

Total Phosphorus, Page 2 of 2

Molybdate/Tartrate Solution. In a 1 liter vol. flask add approx. 600 mls. DI water. Add 8.0 grams Ammonium Molybdate and 0.2 grams Antimony Potassium Tartrate and mix. Fill to volume with DI water and mix. **Make fresh every month.**

Working standards. See digestion procedure.

Quality Control
-Analyze a duplicate every 20 samples. (see QC guidelines)
-Analyze a 2nd Source Std. daily. (±15% recovery or 95% CI)
-Analyze a 4.0 std. at the beginning of each run, at the end of each run and every 10 samples. (Must be ±10% recovery)
-Analyze a matrix spike for every 20 samples (±20% recovery).
-Only use curve points that are ±10% except for the 0.02 which may be 0.01 - 0.03 mg/l.
-8.0 std. must be ±10% recovery to proceed.
-Analyze a digested blank daily. Can be no more that half the reporting level
-Analyze an undigested blank after every 10 samples. Can be no lower than - 0.12 mg/l.
-Holding time is 28 days at 4C.

2

Revision/Review Date: 10/24/13

ORTHO PHOSPHATE AS P
STANDARD METHODS 4500PE-1999

(This method can be found in "Standard Methods for the Analysis of Water and Wastewater, 22nd Edition)

(Make sure you have sufficient quantities of required reagents before beginning analyses)

Use of spectrophotometer: **wavelength = 880 nm** Properly cleaned glassware

1) Turn on spectrophotometer and set wavelength to 880 nm.

2) Rinse enough 125 ml. flasks with DI water to remove any phosphate. If contamination still exists you may need to rinse with hot 50% h2SO4.

3) Measure 50 mls. of sample into a prepared flask using a 50 ml. graduate cleaned as in 2) above. Also prepare a reagent blank, and mid-point QC standard for each curve to be used. (1 cm and/or 5 cm cells) Dilute sample up to 50 mls. with DI water if necessary to fit on calibration curve and note dilution on raw data sheet for proper calculation.

4) Add 1 drop of phenolphthalein indicator. If a red color develops add 5N H2SO4 drop-wise to just discharge color.

5) Add 8.0mls. of combined reagent and mix thoroughly.

6) Adjust the absorbance to 0 with the reagent blank. After 10 minutes but within 30 minutes measure the absorbance at 880 nm. For concentrations from 0 to 0.3 mg/l use 5 cm cell. For concentrations from 0.3 to 0.8 mg/l use 1 cm cell. Dilute any samples which do not fit on curve.

7) For samples high in color perform a background absorbance measurement deleting the ascorbic acid and potassium antimonyl tartrate. Subtract the background values from the sample absorbance values.

8) Determine mg/l values for all samples and standards from calibration curves. Take in to account any dilutions.

Quality Control

-Analyze a blank at the beginning of each run, after every 10 samples, and at the end of the run.
-Analyze a duplicate every 20 samples. Verify duplicates meet established criteria.
-Analyze a curve MID-POINT at the beginning of each run, after every 10 samples, and at the end of the run. Must be +- 10%.
-Analyze a reporting level standard each run. Take corrective action if value is not ± 40% recovery.
-Analyze a 2nd source standard at the beginning of each run. (±10% recovery.)
-Analyze a spike every 20 samples or at least monthly (± 20% recovery).
-Prepare new curve at least annually.
-Holding time is 48 hours at 4C.

Lower Reporting Level: 0.01 mg/l

Prepared by: Steve Jones

OPO4, Page 2 of 3

Reagents

5N Sulfuric Acid. Slowly dilute 70 mls. of conc. Sulfuric Acid to 500 mls. with DI water.
Stable for 6 months.

Potassium Antimonyl Tartrate. To 400 mls. DI water in a 500 ml. volumetric flask add 1.3715 g PAT. Dilute to volume and mix well.

Ammonium Molybdate. To 400 mls. DI water in a 500 ml. volumetric flask add 20g AM. Dilute to volume and mix well.

Ascorbic Acid. In a 100 ml. volumetric flask add 75 mls. DI Water. Dissolve in 1.76 grams of AA. Dilute to volume with DI water and mix well. **Stable for 7 days stored at 4C**

Combined Reagent. Mix the above reagents in the following proportions for 100 ml of the combined reagent: 50 ml 5N Sulfuric Acid
5 ml PAT solution
15 ml AM solution
30 ml AA solution
Mix after the addition of each reagent and mix in the order listed above. Stable for 4 hours.

Stock Phosphorus Solution. In a 1 liter volumetric flask dissolve 0.4393 grams of predried (105C for one hour and dessicated until cool) KH2PO4 in DI water and dilute to 1 liter. **Store at 4C**
1.0 ml = 0.1 mg P = 100 mg/l

Intermediate Phosphorus Solution. In a 500 ml. volumetric flask dilute 5 mls. of stock to 500 mls. with DI water. **1.0 mg/l**

Standard Curves

5 CM CELL (LOW LEVEL) 0 - 0.30 mg/l

mls of inter to 50	mg/l
0.50	0.01
4.00	0.08
5.00	0.10
7.50	0.15
10.0	0.20
15.0	0.30

1CM CELL (HIGH LEVEL) 0.30-0.80 mg/l

mls of inter to 50	mg/l
15.0	0.30
20.0	0.40
25.0	0.50
30.0	0.60
40.0	0.80

***** Make sure all glassware used to make reagents is completely free of phosphate contamination.**

OPO4, Page 3 of 3

Matrix Spike (1 ml = 1 mg P-- Purchased Stock, LabChem or equivalent) 1000 mg/l
LabChem cat# LC18590-1

In a 500 ml volumetric flask add 2.0 ml. stock Matrix Spike and dilute to volume with DI water.
4 mg/l

0.40 mg/l Spike: 5.0 mls. of above solution and dilute to 50 mls. with sample
0.16 mg/l Spike: 2.0 mls. of above solution and dilute to 50 mls. with sample
0.08 mg/l Spike: 1.0 mls. of above solution and dilute to 50 mls. with sample

3

Revision/Review Date: 05/12/14

TOTAL ORGANIC CARBON (TOC & DOC)
Standard Methods 5310C - 2000

(This method can be found on page 5-23 of "Standard Methods for the Examination of Water and Wastewater", 21st Edition Supplement.

Before you begin make sure you have the following:

Sufficient 40 ml vials
Sodium Persulfate reagent
Curve standards and 2nd source standard (ERA, APG, etc.)

1) Remove 1.0 mg/l and 15.0 mg/l standards, 2nd source standard, and samples from the refrigerator and adjust to room temperature.

2) Turn on Nitrogen by turning the top valve 3-4 turns counter-clockwise.

3) Turn of computer and log in as "SJ" (password 123456). Select "Fusion" instrument.

4) Press power button on "Fusion". Make sure wash bottle is full of DI water, Sodium Persulfate is sufficient and Phosphoric Acid is sufficient. Make sure reagent lines are at the bottom of all 3 containers.

5) Perform a "detector offset" and then a "system clean" procedure from the "TOOLS" icon on the toolbar.

6) Select TOC15 as the "Method" to run from the toolbar. This will link with the TOC15 calibrants table with a 5 point curve from 1.0 mg/l to 15.0 mgl.

7) While performing 5) above you can fill out the "Schedule" table for the day's run. Make sure to run a bottle blank, 1.00 mg/l standard, MP 7.50 mg/l standard, and reagent blank at the beginning of the schedule. After every 10 samples run a reagent blank and MP 7.50 mg/l standard. Pour samples in 40 ml. vials and number the corresponding with the numbers in the "Schedule".
All samples must be run in replicate.

8) After the "set baseline" and "clean" have completed, and the schedule is completed, you can start the run.

9) **Observe the run to make sure the blanks and standards are acceptable.**
If not re-calibrate.

Skip to 11) if re-calibration is not required

10) Try re-making either the standard or blank that failed. You may also want to run another "system clean" procedure and/or "detector offset" procedure. If this fails run a new calibrants table.

11) After the run is complete print the data report. Transfer values to the E1 automatic data sheets.

12) Turn off computer, "Fusion", and Nitrogen.

Prepared by: Steve Jones

Page 1 of 3

TOC, Page 2 of 3

Reagents:

Sodium Persulfate Solution (2%). In a 1L. vol. flask add approx. 500 ml DI water. Add 20.0 grams of Potassium Persulfate and 1 ml of Phosphoric Acid. Dilute to mark with DI water.

2000 mg/l Stock TOC. Dry approx. 1 gram of Potassium Hydrogen Phthlate at 104C. Let cool to room temperature in a dessicator. In a 100 ml volumetric flask add approx. 50 ml DI water. Add 0.425 grams of Potassium Hydrogen Phthlate and 0.2 mls of Phosphoric Acid to pH <2. Dilute to mark with DI water.

1.0 mg/l Standard. In a 100 ml volumetric flask dilute 10.0 mls. of 10 mg/l standard and 0.2 mls. phosphoric acid to the mark with DI water.

10 mg/l Standard. In a 200 ml volumetric flask dilute 1.0 ml of 2000 mg/l Standard and 0.4 mls. phosphoric acid to volume with DI water.

15 mg/l Standard. In a 2000 ml volumetric flask dilute 15.00 mls. of 2000 mg/l Standard and 2.0 mls phosphoric acid to volume with DI water.

Bottle Blank. Fill a new 250 ml sample bottle with DI water and add 0.5 mls of phosphoric acid. Mix.

Spike Solution (1000 mg/l). Spike solution must be from a vendor other than the vendor used to produce the curve.

1.0 ml of spike solution to 100 mls sample = 10.0 mg/l spike
0.5 ml of spike solution to 100 mls sample = 5.0 mg/l spike

Quality Control

-Analyze a bottle blank with each sample run.
-Analyze a reagent blank at the beginning of the run, end of the run, and after every 10 samples.

The low standard must be at least 2(1.645)s above the blank.
Therefore, the blank must be 0.300 mg/l or less for a 1.00 mg/l standard.

-Analyze a 2ND source Known with each run. Must be within ±10%.
-Analyze a duplicate every 10 for drinking water samples and every 20 for wastewater samples. Duplicate values should be averaged for reporting. Values must be ± 10% for drinking water and per control charts for wastewater.
-Analyze a 1.0 mg/l and MP 7.50 mg/l standard daily at the beginning of the run. Analyze a MP 7.50 mg/l standard after every 10 samples and 1 at the end of the run. Acceptable value is +-10%.
-Analyze a spike for every 20 wastewater samples (±20% recovery).
-Dilute and re-run any samples which are above 15.0 mg/l.

- Establish MDL values annually.

- Run all samples in replicate, must be ±10% RSD.

Daily calibration may be omitted if standards are within the established acceptance criteria.

TOC, Page 3 of 3

Dissolved Organic Carbon (DOC)

1) Samples must be collected un-acidified. Filter as specified in 2) below within 48 hours of collection and acidify to pH <2.0 with phosphoric acid after filtration. Acidify filter blanks in the same way.

2) Filter samples through 0.45 micron membrane filters. Prepare filter blanks in the same manner for each sample by passing DI blank water through the filter before each sample. Filter a minimum amount of 20 mls. for both sample and blank. **BLANKS MUST BE <0.500 MG/L)**

3) Analyze samples and blanks according to normal TOC procedure.

Review/Revision Date: 05/12/14

DISSOLVED TOTAL ORGANIC CARBON (DDOC) FILTRATION PROCEDURE

Samples must be filtered within 48 hours of collection. Drinking water shipping and receiving will place a note on the bulletin board when samples are in the lab.

Items you will need: 10 ml or 20 ml syringes, 0.45 micron filters, waste beaker, DI water
Phosphoric Acid

1) Remove DDOC samples from refrigerator in Autoclave Room. Complete the DDOC FILTRATION LOG for each sample.

2) Pre-wash each filter with 20 mls of DI water and dispose in waste beaker.

3) Filter approximately 25 mls DI water through the filter and save in 40 ml. vial. Label vial with **"FB"** and the "Sample Number". (This is a filter blank).

4) Shake DDOC sample. With the same filter and syringe you used for the filter blank, filter approximately 25 mls. of sample through the filter saving the filtrate in a separate 40 ml vial. Label vial with the "Sample Number" (This is the filtered sample).

5) Continue on with the remaining samples using a new syringe and filter for each additional filter blank and sample.

6) Add 2 drops of phosphoric acid to each 40 ml vial and place in rack in the refrigerator.

7) Make sure the "Filtration Date" and other sample ID information is listed on the filtration log.

** Every 10 samples must be done in duplicate. Double the amounts filtered in 3) and 4) above. For the DDOC sample filtration you may combine filtrations in a brown amber bottle and pour in to two vials.

Revision/Revision Date: 10/24/13

CARBONACEOUS BIOCHEMICAL OXYGEN DEMAND, 5 DAY)

STANDARD METHODS 5210B - 2001

(This procedure can be found in "Standard Methods, 21, ed, 2001)

THE CARBONACEOUS BIOCHEMICAL OXYGEN DEMAND (CBOD) PROCEDURE IS THE SAME AS A REGULAR 5 DAY BOD EXCEPT THAT NITROGEN INHIBITOR MUST BE ADDED TO ALL SAMPLES AND STANDARDS EXCEPT FOR THE BLANKS AND THAT ALL SAMPLES MUST BE SEEDED.

(A) PRE-ANALYSIS PROCEDURES:

1. DILUTION WATER: USE REGULAR BOD DILUTION WATER.
2. SEED: USE REGULAR BOD POLYSEED.

(B) ANALYSIS PROCEDURE:

1. FOLLOW THE SAME PROCEDURES FOR REGULAR BOD SAMPLES EXCEPT AS NOTED ABOVE.
2. THE DILUTION WATER BLANKS FOR THE REGULAR BODS MAY BE USED FOR QC.
3. AFTER MAKING THE PROPER DILUTIONS ON THE CBOD SAMPLE ADD 0.16G (2 SHOTS) NITRIFICATION INHIBITOR (HACH 2533-35) TO EACH BOD BOTTLE BEFORE ADDING THE AERATED SAMPLE. THE INHIBITOR MUST BE ADDED TO ALL BOTTLES EXCEPT THE BLANKS. **ALL SAMPLES MUST BE SEEDED.**
6. READ THE DO1 FOR EACH BOTTLE AS YOU WOULD FOR REGULAR SAMPLES AND RECORD ON RAW DATA SHEET.
7. AFTER 5 DAYS ± 6 HOURS READ THE DO5 VALUES AND RECORD ON THE RAW DATA SHEET.

REAGENTS

NITRIFICATION INHIBITOR -- HACH #2533-35

QUALITY CONTROL: SAME AS BOD

Prepared by: Steve Jones

Page 1 of 1

1

Revision/Review Date: 12/03/13

BIOCHEMICAL OXYGEN DEMAND (5 DAY)
STANDARD METHODS 5210 B - 2001

(This procedure can be found in "Standard Methods, 21st ed, 2001)

PRE-ANALYSIS PROCEDURE:

1. DILUTION WATER: DILUTION WATER IS TO BE MADE BY ADDING 1 ML EACH OF MAGNESIUM SULFATE, FERRIC CHLORIDE, CALCIUM CHLORIDE, AND PHOSPHATE BUFFER TO EACH LITER OF DEIONIZED WATER USED. DILUTION WATER IS TO BE MADE THE SAME DAY IT IS TO BE USED. THE ELEVATED WATER TANK IS TO BE CLEANED BEFORE USE EACH DAY.

2. DILUTION WATER CHEMICALS: ALL DILUTION WATER CHEMICALS ARE PRE-MADE SOLUTIONS FROM FISHER SCIENTIFIC. AS WITH ALL OTHER CHEMICALS, THE FOUR USED WITH DILUTION WATER ARE TO BE DATED WHEN THEY ARE OPENED AND THE EXPIRATION DATE CHECKED. AFTER OPENING STORE THE PHOSPHATE BUFFER SOLUTION IN THE REFRIGERATOR. THE PH OF THE PHOSPHATE BUFFER MUST BE 7.2 ± 0.2 AND RECORDED IN LOG BOOK.

3. SEED: "SEED" IS THE TERM USED FOR A SOURCE OF BACTERIA THAT IS ADDED TO CERTAIN SAMPLES WHICH HAVE NO BACTERIA DUE TO ABNORMAL PH, INDUSTRIAL WASTES, STERILIZATION OR CHLORINATION. THE SEED WE USE IS POLY SEED. TO BEGIN EACH DAY OPEN A CAPSULE OF POLY SEED AND, USING A GRADUATED CYLINDER, DISSOLVE CAPSULE IN THE REQUIRED AMOUNT OF **DILUTION WATER**. PLACE ON A STIR PLATE WITH MAGNET AND AERATION, LET IT MIX FOR AT LEAST 1 HOUR. LET SETTLE AND DECANT BEFORE USING. ALWAYS MIX THE SOLUTION AS YOU REMOVE ANY FOR SEEDING PURPOSES. THE AMOUNT ADDED, CALLED THE "SEED RATE" IS DETERMINED BY THE ANALYST BY USING PAST HISTORY. AN AMOUNT OF SETTLED AND FILTERED DOMESTIC INFLUENT MAY BE ADDED TO THE POLYSEED IF NEEDED. ADD THE DATE THE INFLUENT WAS FILTERED TO THE END OF THE POLYSEED LOT NUMBER ON THE RAW DATA FORM.

4. LDO PROBE MAINTENANCE: CHANGE THE SENSOR CAP AND STIR ROD AS NEEDED.

DILUTION WATER TANK/JUG CLEANING PROCEDURE:

THE VARIOUS TANKS AND JUGS THAT ARE USED TO MIX AND STORE DILUTION WATER PROVIDE EXCELLENT GROWING CONDITIONS FOR BACTERIA AND GROWTHS WILL BUILD WHICH COULD SLOUGH-OFF AND AFFECT THE D.O. DEPLETION OF A SAMPLE. THIS BUILD UP OF BACTERIAL GROWTHS MUST BE PREVENTED BY REGULAR CLEANING OF THESE TANKS, JUGS AND TUBING.

WEEKLY CLEANING/STERILIZATION: ONE DAY EACH WEEK ADD 100 MLS OF CHLORINE TO EACH TANK OR JUG FOR EACH 5 GALLONS OF CAPACITY AND FILL WITH TAP WATER. AFTER LETTING SET FOR A FEW MINUTES RINSE WITH TAP WATER THROUGHLY TO REMOVE ALL TRACES OF CHLORINE AND THEN RINSE WITH DI WATER. CLEAN AIR PUMP TUBING OR REPLACE AS NEEDED.

ANALYSIS PROCEDURE:

1. METER WARM-UP/SEED PREPARATION: THE LDO METER MUST BE WARMED AT LEAST 5 MINUTES IN ORDER FOR THE ELECTRONICS TO STABILIZE. PREPARE POLY SEED AS DESCRIBED ABOVE.

Prepared by: Steve Jones

BOD, Page 2 of 5

2. WARMING OF COLD SAMPLES: THE TEMPERATURE OF THE FINAL WATER THAT IS PUT IN THE BOD BOTTLES WILL DRASTICALLY AFFECT THE D.O. THAT IS READ. THEREFORE, AN EFFORT IS MADE TO HAVE THE SAMPLES, DILUTION WATER AND SEED AT OR NEAR 20 C. THE DILUTION WATER WILL ALREADY BE APPROX. 20 C AND THE SEED REPRESENTS SUCH A SMALL PERCENTAGE OF THE TOTAL THAT IT DOES NOT AFFECT TEMPERATURE. THE SAMPLE ITSELF, HOWEVER, REPRESENTS A SIGNIFICANT PORTION OF THE TOTAL AND USUALLY COMES TO US ICED DOWN. THEREFORE, ALL BOD SAMPLES ARE TO BE WARMED (IF NEEDED) IN A **WARM (TEPID)** WATER BATH OR OTHERWISE BROUGHT TO NEAR 20 C BEFORE ANALYZING.

3. GETTING LDO METER ON LINE: THE LDO METER SHOULD BE WARMED BY THIS TIME. FOLLOW THE INSTRUCTIONS FOR CALIBRATION NEXT TO THE METER

4. LDO METER CALIBRATION: CALIBRATE AS PER INSTRUCTIONS SUPPLIED BY HACH. CLEAN THE PROBE WITH DI WATER. LET THE PROBE STABILIZE 5 MINUTES AND PERFORM THE AIR CALIBRATION PROCEDURE. AFTER AIR CALIBRATION PLACE THE PROBE IN THE FIRST DO1 BLANK BOTTLE AND TURN STIRRER ON. LET STABILIZE BEFORE READING. READ THE REMAINING TWO BOD BLANK BOTTLES. IF ALL THREE BLANKS ARE NOT WITHIN 0.1 MG/L OF EACH OTHER DISCARD ALL THREE BLANKS AND PERFORM THE BLANK PROCEDURE AGAIN.

5. PREPARATION OF BLANKS: AFTER THE DILUTION WATER HAS BEEN PUMPED INTO THE ELEVATED STORAGE TANK, ABOUT 1 LITER SHOULD BE DRAINED TO THE SINK TO CLEAR THE LINES. FILL A 1 GALLON PLASTIC BOTTLE WITH DILUTION WATER TO BE USED FOR SAMPLE DILUTIONS. AFTERWARDS, DRAW OFF THREE BLANKS IN SUCCESSION. PLACE BLANKS IN SONIC BATH. READ THE INITIAL DO1 VALUES TO TWO DECIMAL PLACES FOR ALL THREE AND RECORD ON RAW DATA SHEET. INCUBATE THE 3 BLANKS FOR 5 DAYS AND MEASURE AND RECORD DO5 VALUES TO TWO DECIMAL PLACES.

6. UNSEEDED SAMPLES: ALL DILUTIONS ARE TO BE MADE FROM THE CHART ON THE WALL UNLESS OTHERWISE SPECIFIED. SET AT LEAST TWO DILUTIONS ON EACH SAMPLE IF IT IS A REGULAR CLIENT YOU FEEL CONFIDENT WITH. ONE DILUTION (100%) MAY BE SET ON STREAMS UNLESS THEY APPEAR TO BE OUT OF THE ORDINARY, IN WHICH CASE YOU SHOULD SET A 50% DILUTION. IN THE WINTER MONTHS IT MAY BE NECESSARY TO AERATE SOME SAMPLES MORE VIGOROUSLY TO REDUCE THE INITIAL D.O. TO LESS THAN 9 MG/L. IT MAY ALSO HELP TO LEAVE THE SAMPLES IN THE WARM WATER LONGER TO REDUCE THE INITIAL D.O. TO BETWEEN 7-9 MG/L. ADD 1.2 MLS. OF NUTRIENT SOLUTION TO ALL 100% SAMPLES.

7. SEEDED SAMPLES: SAMPLES ARE SEEDED WHEN THERE IS NO BACTERIA PRESENT DUE TO ABNORMAL pH, CHLORINATION, OR INDUSTRIAL SAMPLES. ADJUST ALL SAMPLES TO A NEUTRAL pH IF THE SAMPLE pH IS LESS THAN 6.0 OR GREATER THAN 8.5 UNITS (ADJUST SAMPLES TO PH 6.5 - 7.5). ADD 1.2 MLS. OF NUTRIENT SOLUTION TO ALL 100% SAMPLES. SET AT LEAST TWO DILUTIONS, MORE IF IT IS A NEW CLIENT. THE SAME PROBLEM MAY EXIST WITH HIGH INITIAL D.O. VALUES IN THE WINTER MONTHS. FOLLOW THE SAME PROCEDURES LISTED ABOVE TO REDUCE THE D.O. TO BETWEEN 7-9 MG/L.

CHECK AND NEUTRALIZE FOR CHLORINE USING THE FOLLOWING PROCEDURE:

1) MEASURE 50 MLS. OF SAMPLE INTO THE ERLENMEYER FLASK
2) ADD 5 MLS. OF POTASSIUM IODIDE
3) ADD 5 MLS. OF 1 + 50 SULFURIC ACID SOLUTION
4) SHAKE, THEN ADD ONE SQUIRT OF STARCH
   IF BLUE COLOR IS PRESENT (CHLORINE) PROCEED WITH #5
   IF CLEAR YOU MAY STOP
5) TITRATE DROPWISE WITH .025 NORMAL SODIUM SULFITE
6) AMOUNT OF SULFITE TO ADD TO SAMPLE =
   (MLS. SAMPLE / 50) X MLS. OR DROPS TITRANT USED
7) NEUTRALIZE THE REMAINING SAMLE AND RECORD INFORMATION ON SHEET

2

YOU MAY SCREEN SAMPLES FOR CHLORINE BY USING THE FOLLOWING PROCEDURE:

TEST ABOUT 5 MLS WITH ONE SQUIRT OF POTASSIUM IODIDE AND ONE SQUIRT OF STARCH. A POSITIVE TEST WILL TURN BLUE. ANY THAT ARE POSITIVE MUST BE CARRIED THRU THE ABOVE NEUTRALIZATION PROCEDURE.

IF MORE THAN 45 MLS OF SODIUM SULFITE WILL BE NEEDED TO NEUTRALIZE 900 MLS. OF SAMPLE USE DOUBLE STRENGTH SODIUM SULFITE (.050N) AND USE I/2 AS MUCH AS CALCULATED TO NEUTRALIZE SAMPLE.

EXAMPLE: YOU CALCULATE THAT IT WILL TAKE 50 MLS. OF THE 0.25N, THEN YOU WILL NEUTRALIZE USING 25 MLS OF THE 0.50N.

THIS PREVENTS DILUTING THE SAMPLE BY MORE THAN 5%.

FOR SAMPLES WHICH NEED TO BE SEEDED, ADD THE REQUIRED AMOUNT OF POLYSEED SOLUTION DIRECTLY TO EACH BOD BOTTLE. THIS AMOUNT WILL BE THE SAME FOR ALL SEEDED SAMPLES INCLUDING THE GG STANDARDS.

8. SAMPLE ANALYSIS

A) <u>DIRECT BOTTLE METHOD</u>. LINE UP SAMPLES ON COUNTER. **IMMEDIATELY BEFORE MEASURING OR PIPETING SHAKE ALL SAMPLES THOROUGHLY!!!.** ADD SAMPLE DIRECTLY IN TO BOD BOTTLES. USE SAMPLE TABLES TO DETERMINE PROPER AMOUNTS. ADD SEED IF REQUIRED AND FILL BOD BOTTLE WITH DILUTION WATER. MAKE SURE CLIENT NAME, BOTTLE NUMBER, CLIENT NUMBER, SAMPLE DATE, LOCATION CODE, AND % SAMPLE ARE RECORDED ON THE RAW DATA SHEET. SONICATE ALL SAMPLES BEFORE READING DO1 VALUES. READ D.O. 1 VALUES AND STOPPER EACH BOTTLE IMMEDIATELY AFTER D.O. DETERMINATION, PLACE WATER SEAL IN LIP OF BOTTLE, AND CAP WITH PLASTIC COVER. AFTER EACH 20 BOD BOTTLES CHECK FOR DRIFT OF THE LDO METER. RE-CALIBRATE IF READING IS NOT ± 0.20 MG/L. REMEMBER TO RINSE THE 1 LITER GRADUATES BETWEEN SAMPLES IF MORE THAN 201 ML. OF SAMPLE US USED (100% DILITIONS) THEN 1.2 MLS OF THE NUTRIENT SOLUTION MUST BE ADDED TO THE BOTTLE.

B) <u>DILUTION METHOD</u>. LINE UP SAMPLE BOTTLES ON THE COUNTER. PLACE THE REQUIRED NUMBER OF 1 LITER GRADUATES BEHIND EACH SAMPLE. **SHAKE ALL SAMPLES THOROUGHLY!!! IMMEDIATELY BEFORE POURING** MEASURE THE PROPER AMOUNT OF SAMPLE GIVEN IN THE TABLE USING THE PLASTIC GRADUATES INTO THE 1 LITER GRADUATES. FILL TO THE 400 ML. MARK WITH REGULAR DILUTION WATER. AERATE THE SAMPLES WITH THE PLASTIC WAND USING EIGHT EVEN STROKES GOING FROM THE WEAKER TO THE STRONGER DILUTION. RINSE THE PLASTIC WAND IN A FLOWING WATER BATH BETWEEN EACH SET OF SAMPLES. POUR THE SAMPLE INTO B.O.D. BOTTLES WITHOUT OVERFLOWING. AERATE AND POUR SAMPLES HIGH IN SOLIDS AT ONCE. MAKE SURE CLIENT NAME, BOTTLE NUMBER, CLIENT NUMBER, SAMPLE DATE, LOCATION CODE, AND % SAMPLE ARE RECORDED ON THE RAW DATA SHEET. MEASURE THE D.O. OF EACH BOTTLE AND RECORD ON THE DATA SHEET, THIS WILL BE THE D.O. 1 VALUE. STOPPER EACH BOTTLE IMMEDIATELY AFTER D.O. DETERMINATION, PLACE WATER SEAL IN LIP OF BOTTLE, AND CAP WITH PLASTIC COVER. AFTER EACH 20 BOD BOTTLES CHECK FOR DRIFT OF THE LDO METER. RE-CALIBRATE IF READING IS NOT ± 0.20 MG/L. REMEMBER TO RINSE THE 1 LITER GRADUATES BETWEEN SAMPLES. FOR 100% SAMPLES 1.2 MLS OF THE NUTRIENT SOLUTION MUST BE ADDED TO THE BOTTLE.

GG STANDARDS DUPLICATE GG STANDARDS ARE TO BE SET WITH EACH DAY'S SAMPLES. FOR HACH STANDARD, LAB-CHEM STANDARD, OR LAB PREPARED STANDARD, PIPET 6.0 MLS USING A **VOLUMETRIC PIPET**. ADD THE SAME AMOUNT OF SEED SOLUTION USED FOR SEEDED SAMPLES TO EACH BOD BOTTLE. FILL TO TOP WITH DILUTION WATER. READ AND RECORD DO DATA ON RAW DATA SHEET.

SEED STRENGTH DETERMINATION: SET 2 DILITIONS ON THE SEED SOURCE ACCORDING TO PAST HISTORY. ADD THE PROPER AMOUNT OF SEED SOLUTION DIRECTLY TO THE BOD BOTTLES AND FILL WITH REGULAR DILUTION WATER. READ AND RECORD DO DATA ON RAW DATA SHEET.

DO 5: AFTER FIVE DAYS ± 6 HOURS THE SAMPLES MUST BE REMOVED FROM THE INCUBATOR AND THE D.O. READ AGAIN. LET LDO METER WARM UP FOR AT LEAST 5 MINUTES TO STABILIZE THE ELECTRONICS. TAKE OUT THE 3 REMAINING BLANKS THAT WERE SET UP 5 DAYS EARLIER ALONG WITH THE SAMPLES. FOLLOW THE SAME PROCEDURES OUTLINED ABOVE FOR METER SET-UP AND CALIBRATION. UNCAP, POUR OFF WATER SEAL, AND REMOVE THE STOPPERS. STARTING WITH THE BLANKS, STANDARDS, THEN SAMPLES READ THE D.O. AND RECORD THE RESULT IN THE DO5 COLUMN ON THE ORIGINAL SAMPLE DATA SHEET. AFTER 20 SAMPLES CHECK METER FOR DRIFT AND RE-CALIBRATE IF READING IS NOT ± 0.20 MG/L. RE-READ ANY SAMPLES THAT WERE READ BEFORE THE DRIFT READING WAS MADE IF NOT WITHIN RANGE.

REAGENTS

ALL REAGENTS ARE FISHER PURCHASED REAGENTS EXCEPT THE FOLLOWING:

GG STANDARD. USE HACH OR LAB CHEM STANDARD WHEN POSSIBLE. IF UNAVAILABLE, DRY REAGENT-GRADE GLUCOSE AND REAGENT-GRADE GLUTAMIC ACID AT 103 C FOR 1 HOUR. IN A 1 LITER VOLUMETRIC FLASK ADD 0.150 GRAMS GLUCOSE AND 0.150 GRAMS GLUTAMIC ACID TO APPROXIMATELY 800 MLS. DEIONIZED WATER. DILUTE TO VOLUME AND MIX WELL. **198 MG/L + 30.5**

POTASSIUM IODIDE SOLUTION. PURCHASED FROM FISHER SCIENTIFIC (CAT # LC19760-4).

HACH GG STANDARD. DILUTE 1 TO 1 WITH DI WATER. USE 6.0 MLS PER BOTTLE TO YIELD **198 MG/L +- 30.5 .**

LAB-CHEM GG STANDARD. PURCHASED AT CORRECT CONCENTRATION. USE 6.O MLS PER BOD BOTTLE TO YIELD **198 MG/L +- 30.5.**

STARCH SOLUTION. BRING 3.5 L. DI WATER TO A BOIL. ADD 20 GRAMS OF STARCH (FISHER #S516-100) AND 5 GRAMS OF SALICYLIC ACID (FISHER # A277-500). BOIL UNTIL DISSOLVED AND ALLOW TO SIT OVER NIGHT. DILUTE TO 4.0 LITERS WITH DI WATER AND MIX.

1+50 SULFURIC ACID SOLUTION. DILUTE 20 MLS H2SO4 TO 1 LITER WITH DI WATER.

Sodium Sulfite Solution This solution is used to neutralize chlorine.

1) In a 1 liter volumetric flask add 1.575 grams of Sodium Sulfite to approx. 800 mls. of DI water.
2) Dilute to volume with DI water and mix well.
3) Make this solution daily.

Nutrient Solution for 100% samples. Add 10 mls. of each of the 4 nutrients to a beaker and mix. To each 100% BOD sample add 1.2 mls. of this solution to the BOD bottle before adding the sample.

4

QUALITY CONTROL

Analyze a duplicate GG with each day's run. Must be 167.5 – 228.5 mg/l. If outside this range then the data must be qualified.

Analyze a duplicate sample for each 20 samples. Verify duplicates meet the established criteria of ±30%. If not the duplicates data must be qualified.

DO drop on blanks should be 0.20 or less after 5 days. If outside this range then the data must be qualified.

Seed Correction Factor (SCF) can be no higher than 1.4 mg/l.

Analyze a "seeded blank" daily. Record on raw data sheet.

Samples must be read at 5 days ± 6 hours.

Use "air calibration" method as per HACH LDO manual.

Perform drift checks as needed . Make sure to perform a drift check after the final BOD and CBOD samples recorded on the raw data sheets each day. Drift checks must be performed for day one (DO1) and day five (DO5) readings.

Record all reagents or dilution water made in a log book.

At the end of each day clean the Polyseed solution beaker with micro and hot tap water. Let this sit for about 15 minutes; then rinse with DI water several times. Turn beaker upside down and place on a clean paper towel to dry.

Drain the dilution water tank daily. Rinse with tap water and then rinse with DI water.

Holding time for BOD samples is 48 hours at 4C.

Maintain dilution water at 20C ± 2 degrees.

Frozen Seed Supplement. Record source, date filtered, amount added to POLYSEED, and lot number of POLYSEED in Steve's log book.

Review/Revision Date: 10/24/13

CHLORINE NEUTRALIZATION PROCEDURE FOR BOD SAMPLES

1) Measure 50 mls. of sample using a graduated cylinder in to an Erlenmeyer flask

2) Add 5 mls. Of Potassium Iodide (10%) and mix.

3) Add 5 mls. of 1+50 Sulfuric Acid solution and mix.

4) Add 1 ml. (1 squirt) of starch solution and mix.

5) Titrate drop wise to clear end-point with 0.025N Sodium Sulfite. (If it only takes 1 drop stop here). **Use double strength Sodium Sulfite (0.050N) for samples if more than 45 mls of regular Sodium Sulfite will be needed to neutralize 900 mls. of sample. This prevents diluting the sample by more than 5%.**

6) Amount of Sodium Sulfite added to sample = (mls. sample/50) x mls. or drops of titrant used.

7) Pour remaining sample in 1 liter graduate and neutralize.

8) A neutralization sheet is to be used to record the following information:

   a) Client ID #
   b) Sample volume
   c) Chlorine present
   d) Mls. or drops of titrant required to neutralize the 50 ml. test volume
   e) Mls. of drops of titrant required to neutralize the sample volume

9) Rinse the Erlenmeyer flask and graduate with deionized water between samples.

Reagents:

1+50 Sulfuric Acid Solution. 20 mls. H_2SO_4 to 1 liter with DI water.

Starch Solution. Bring 3500 mls. DI water to a boil. Add 20 grams of starch. (Fisher #S516-100) and 5 grams of Salicylic Acid (Fisher #A277-500). Boil until dissolved. Allow to sit overnight. Dilute to 4 liters with DI water and mix.

Standard Sodium Sulfite . Dilute 1.575 grams to 1 liter with DI water. (0.025N)

Sodium Sulfite (Double Strength). Dilute 3.150grams to 1 liter with DI water. (0.050N)

Potassium Iodide. Purchased from LabChem (#LC-19760-4)

Prepared by: _____
Steve Jones

Page 1 of 1

<stat.BOD>

BOD STATISTICAL QUALITY CONTROL GUIDELINES

SM 5210B

If any of the following quality control failures occur the data must be qualified on the client result sheets.

1) No sample dilutions deplete at least 2.0 mg/l DO and have a residual of at least 1.0 mg/l DO (unless 100% sample is analyzed).

2) The dilution water blank is greater than 0.20 mg/l.

3) The GGA check standard falls outside the acceptance limits of 198 mg/l ± 30.5 mg/l (167.5 - 228.5 mg/l). The average of multiple GGA standards must be within the acceptance limits.

4) Duplicate results must be qualified if they vary by more that 30% between high and low values.

   Calculation: 1 - (low value/high value) x 100

   Example: BOD Dilution 1 = 4.5
   BOD Dilution 2 = 5.2

   [1- (4.5/5.2)] x 100 = 13.5%

5) No Seed control dilutions deplete at least 2.0 mg/l DO and have a residual of at least 1.0 mg/l DO.

Corrective Actions

1) Review method and SOP.
2) Review sample mixing and measuring procedures.
3) Work with a more experienced analyst if problems persist.

Revision date: 07/08/14

Chlorophyll-a
EPA Method 445.0

• Chlorophyll-a Filtration Procedure:

1. Initial Procedures:

a. At 8:00 AM (Monday through Friday) and at 4:30 PM on Friday, check the Chlorophyll-a refrigerator for samples. If any are there, take them to the sample prep area for initial pH check and filtering.

b. Fill the DI water squeeze bottle with DI water.

c. Set up the sample prep area as a darkroom (lower shade to AA room, place note on door, unplug Exit light, cut on green light, close all doors, cut off all overhead lights).

d. Set up small test tubes in the foam support, and with only the green light on, uncap the bottles and pour sample from each bottle into a corresponding test tube.

e. Place the caps back on the bottles, cut on the overhead lights and check the pH of the samples in the test tubes using pH test strips. If the pH is 7 or greater, continue with step 2 below. If the pH is less than 7, filter sample and complete entire process as soon as possible.

2. Filter Apparatus Set-up and Vacuum Adjustment:

a. Empty the Erlynmeyer Flask contining the waste water.

b. Line up the samples and an empty petri dish in front of each sample filter. Number each petri dish and sample bottle starting with the next available number on the current Chlorophyll-a bench sheet. (use the current color being used, either black or red).

c. Fill in the information on the bench sheet (from Client Name through Location Code) for each sample.

d. Cut off the overhead lights so that the area is once again a darkroom with green light.

e. Place a Whatman GF/F filter on the right most filtering funnel. Add about ¼ in of DI water to the filter to wet it.

Prepared by: M. Oli
Mark Oliveira

f. Cut on the vacuum pump and open the valve on the funnel to filter the water through.

g. Note the vacuum gauge reading... it should be approximately 5. If not, adjust the control knob on the gauge to fine-tune the vacuum (and the left most filter valve for a coarse adjustment, if necessary).

3. Sample Filtration:

a. Mix the first sample by gently inverting the sample bottle several times. Pour 150 mls of sample into a graduated plastic cylinder.

b. With the filter valve closed, cut on the vacuum pump, pour about 50 mls into the filter funnel, and then open filter valve and watch as the water is pulled through. Note two things:

   1. The vacuum gauge should still be at around 5, and

   2. Close the filter valve just before the entire sample is sucked through so that about ¼ in. of water is left in the filter funnel.

c. Repeat with another 50 ml portion of sample, again checking the vacuum gauge and not letting all of the sample be sucked through.

d. As the filter becomes more plugged, each addition of sample will pass through more slowly. The analyst must use his/her judgment as to when to stop adding sample. Normally, you will add smaller and smaller portions as the filter becomes more and more plugged. When you decide to stop adding sample, watch the sample level carefully as it falls in the filter. With your hand on the filter valve, close it slowly as the water level is approaching dryness, then cut it off quickly as the last amount of sample passes through.

e. Unscrew the filter unit and using tweezers, carefully remove the GF/F filter disk and place it in the appropriately numbered petri dish.

f. **(Duplicate)** For each 10 samples, a duplicate is filtered. Repeat the procedures in a.- e. above for one of the samples already filtered. Mark the petri dish with the duplicate number such as DUP1, DUP2, etc.

g. **(Laboratory Reagent Blank)** For each day's filtration a Laboratory Reagent Blank must be filtered. For a blank, repeat the procedures in a.- e. above but use 1000 ml of D.I. water as the sample. Mark the petri dish as appropriate with LRB1, LRB2, etc.

h. Repeat procedures in a.- e. above for each of the other samples. When finished, place all of the petri dishes on a large piece of aluminum foil and wrap securely. Mark the foil with red or black pens as appropriate. Place the aluminum wrapped petri dishes in the freezer at -20 deg. C. as soon as possible.

• Chlorophyll Extraction Procedure:

1. Holding Time Considerations:

a. The filter pads which have previously had sample passed through can be held frozen and wrapped in aluminum foil for 3.5 weeks, however to provide a margin of safety we will keep the oldest sample frozen for approximately two weeks before extracting the filters.

b. The analyst should refer to the date when the oldest sample was filtered, and be prepared to perform the extraction process on the Tuesday morning which is closest to two weeks from the date of that oldest sample.

c. Several days before you will be doing the extractions, inform sample prep and AA areas (they also use the sample prep room and may need to adjust their schedules).

d. They also have samples which will be set in the sample prep room. You should start setting up your equipment and getting your supplies ready about 8:30 AM, working around them as best you can. However, start your dark room extraction **no later than 9:00 AM**

e. The third and final part of the Chlorophyll-a test (Flurometer) must be done about 24 hours after the extraction part of the test. Therefore, you should check with Wet Chem the day before to be certain they will be prepared to do their part on Wednesday morning

2. Initial Procedures:

a. 90% Acetone Reagent: 90% Acetone Reagent is kept in a 1 liter squeeze bottle with red tape and is used in the extraction process. When more needs to be made, use the 1 liter graduate cylinder with the ground glass stopper. Prepare by pouring reagent grade Acetone into the graduate up to the 900 ml mark, then fill to the 1000 ml mark with D.I. water. Insert the glass stopper and mix well by inverting and shaking vigorously several times. If all of the 1000 ml is not needed to fill the squeeze bottle, the excess can be left in the graduate with the glass stopper inserted and used at a later time.

b. In the end of the fume hood located closest to the outside door, set up two green lights and the drill with tissue grinder.

c. Obtain the following:
   1. an adequate number of 50 ml plastic centrifuge tubes (AA room)
   2. two plastic tube racks

3. a black felt tip pen
4. a squeeze bottle of 90% Acetone
5. tweezers
6. glass rod
7. glass grinding tube
8. roll of aluminum foil.
9. small cardboard box

e. Carry the frozen filter plates wrapped in aluminum foil from the freezer to the darkroom.

d. Set up the sample prep area as a darkroom (lower shade to AA room, place note on door, unplug Exit light, cut on green light, close all doors, cut off all overhead lights).

3. Extraction Procedures

a. Take the foil off of several petri dishes and allow them to warm at room temperature.

b. Using the felt tip pen, write the ID number for the petri dish you are extracting to a plastic centrifuge tube. Place the tube in the rack.

c. Using a pair of tweezers, remove the first filter pad from the plate, and using another pair of tweezers, tear the filter in half. Then using the tweezers, tear each half into quarters. Place all of the quarter pieces into the glass grinding tube and use the glass rod to push each piece of filter to the bottom of the tube.

d. Using 90% acetone, rinse down the side walls of the glass grinding tube until approximately 10 mls has been added.

e. Start the drill on a slow speed and push the glass grinding tube containing the filter pieces and Acetone up on the tissue grinder. Move the glass tube in and out, being careful not to let the Acetone get warm due to the friction.

f. Most, but not all of the filter paper will be ground into a slurry. After grinding, slowly remove the tissue grinder and rinse it with 90% Acetone into the glass grinding tube.

g. Pour the contents of the glass grinding tube into a labeled plastic centrifuge tube. You may have to use the glass rod to assist in transferring the pulp from the glass tube to the centrifuge tube. Continue washing the glass grinding tube with small portions of the 90% Acetone and transferring them to the centrifuge tube until all of the pulp has been transferred to the centrifuge tube.

h. Continue washing the glass tube and transferring to the centrifuge tube until the Acetone level in the centrifuge tube is just below 25 ml. At this point, slowly add 90% Acetone to the centrifuge tube until the level reaches 25 ml.

i. Cap the centrifuge tube tightly and shake vigorously. There should be no leaking around cap. Place the tube in the rack.

j. After grinding all of the samples, wrap each of the centrifuge tubes with aluminum foil and place in the cardboard box. Pack paper around the tubes so as to keep them standing upright in the box. Place the box of tubes in the **refrigerator** (not the freezer).

k. Write the Sample Extraction Date on the filter bench sheets.

• Chlorophyll-a Analysis:

NOTE: Analysis is completed using the Turner Trilogy Fluorometer with the Chlorophyll-a non-acidification module (narrow band pass filter).

1. Set up the Fluorometer in the Hot Room. Turn on both the Fluorometer and Spectrophotomer using the switches on the rear and allow to warm up.

2. Set up the Hot Room as a darkroom (set up 3 green lights, cover window in door, place note on door, cut off all overhead lights).

3. Check to be certain that room is dark by cutting off all green lights to verify that you are in complete darkness.

4. Obtain the box of standards from the freezer and carry to the Hot Room. Remove the identification tags from the bottles marked QCS Intermediate Stock, High Standard and Low Standard (leaving the QCS Primary Standard in the box… it will not be used). Unwrap the foil from the bottles and leave them sitting out to warm to room temperature (place on counter in front of fan to assist in warming the bottles).

5. Transfer the following from the sample prep room to the Hot Room:
   a. Squeeze bottle containing 90% Acetone
   b. 100 ml volumetric flask
   c. 2.5 ml volumetric pipet
   d. 5 cm cells
   e. Calculator
   f. Rubber bulb pipets
   g. Blue rubber bulb
   h. Foam block with four small vials
   i. Box of small screw-cap vials
   j. Bench Sheets
   k. Roll of Aluminum foil
   l. Plastic racks

6. Remove the samples (foil covered tubes) from the refrigerator and carry them to Hot Room. Remove the aluminum foil from each of them. Find all of the LRB samples and place them, plus other samples so as to make a full rack, in the centrifuge. **Make certain that the number of tubes on each side of the rotor are the same so as to assure balance!** Set speed to 7 and timer to 15 minutes. The centrifuge will accommodate 8 tubes. Depending on the number of samples, this may take more than one run, however you can be working on the 1st batch while another batch is spinning.

7. The standards will need about 15 minutes to come to room temperature. Use this time to centrifuge samples. When the standards are at room temperature, proceed with the Spectrometer and Fluorometer calibrations below.

A. Spectrometer Calibration:

REAGENTS:

1. QCS Primary Standard Preparation

Note: This standard is kept wrapped in Aluminum foil and stored in the freezer, it only needs to be prepared about every 9 months. The tag on the bottle will list the date it was made. Prepare as below only if needed:

In the green light darkroom, fill a **200 ml** volumetric flask about 1/2 full with 90% Acetone. Place a glass funnel in the flask. From the freezer, open a vial of Sigma Chlorophyll-a (Catalog #C6144-1mg). Dump the contents of the vial into the funnel and wash down the vial with 90% Acetone. Wash several additional times, finally washing down the glass funnel. Fill the flask to the mark with 90% Acetone, cap and shake well. Wrap the flask in aluminum foil and let sit for about an hour for the Chlorophyll-a to dissolve. After an hour, remove the foil under green light and verify that it is completely dissolved. Pour all of the standard into a brown glass bottle, date the tag on the bottle. Wrap in aluminum foil and store in the freezer.

2. QCS Intermediate Standard Preparation *(the actual value of this standard will vary depending on the concentration of the QCS Primary Standard from which it is prepared.)*

Note: This standard is kept wrapped in Aluminum foil and stored in the freezer, it only needs to be prepared every three months. The tag on the bottle will list the date it was made. Prepare as below only if needed:

In the darkroom, fill a **100 ml** volumetric flask about 1/2 full with 90% Acetone. Using a 30 ml volumetric pipet, add 30 mls of the Primary Standard to the flask, finish filling to the mark with 90% Acetone, cap and shake well to mix. Pour all of standard into a brown glass bottle, date the tag on the bottle.

3. 90% Acetone Reagent:

90% Acetone Reagent is kept in a 1 liter squeeze bottle and is used in the extraction process. When more needs to be made, use the 1 liter graduate cylinder with the ground glass stopper. Prepare by pouring reagent grade Acetone into the graduate up to the 900 ml mark, then fill to the 1000 ml mark with D.I. water. Insert the glass stopper and mix well by inverting and shaking vigorously several times. If the full 1000 ml is not needed to fill the squeeze bottle the excess can be left in the graduate with the glass stopper inserted.

4. Fill one of the 5 cm cells with 90% Acetone (this is the blank), clean the cell windows with Acetone wetted paper towels.

5. Fill the other 5 cm cell with QCS Intermediate Standard (this is the standard), clean the cell windows with Acetone wetted paper towels.

6. Set the Spectrometer to a wavelength of 750 as follows:

   a. From the keypad, enter "7-5-0", then press "Second Function", then press "Yes".
   b. Insert the Blank cell.
   c. From the keypad, press "Second Function", then press "%T/A/C".
   d. When display reads 0.000, remove Blank cell and insert Standard cell.
   e. Record absorbance reading on Spectrometer Calibration sheet.

   (Note: Absorbance should be between 0.000 and 0.005 for the 750 wavelength, but will be different for the other wavelengths)

7. Repeat the steps for the following wavelengths:

   664 nm: From the keypad, enter "6-6-4", then press "Second Function", then "Yes". Insert the Blank cell. From the keypad, press "Second Function", then press "%T/A/C". When the display reads 0.000, remove the Blank cell and insert the Standard Cell. Record the absorbance reading on the Spectrometer Calibration sheet.

   647 nm: From the keypad, enter "6-4-7", then press "Second Function", then "Yes". Insert the Blank cell. From the keypad, press "Second Function", then press "%T/A/C". When the display reads 0.000, remove the Blank cell and insert the Standard Cell. Record the absorbance reading on the Spectrometer Calibration sheet.

   630 nm: From the keypad, enter "6-3-0", then press "Second Function", then "Yes". Insert the Blank cell. From the keypad, press "Second Function", then press "%T/A/C". When the display reads 0.000, remove the Blank cell and insert the Standard Cell. Record the absorbance reading on the Spectrometer Calibration sheet.

8. Complete the calculations on the Spectrometer Calibration sheet.

10. Rinse the standard cell three times with 90% Acetone. Discard the 90% Acetone from the blank cell. Leave both cells sitting out to dry.

B. Fluorometer Calibration:

REAGENTS:

Working QCS Standard: *(the actual value of this standard will vary depending on the concentration of the QCS Primary Standard from which it is prepared.)* Prepare the standard by filling a 100 ml volumetric flask about ¾ full with 90% Acetone. Using a 2.5 ml volumetric pipet, add 2.5 mls of the QCS Intermediate Standard to the flask, finish filling to the mark with 90% Acetone, cap and shake **very** well to mix. Prepare fresh daily.

1. Fill the four glass Fluorometer vials as follows:

   a. Using a rubber bulb pipet, fill the "HS Vial" with the high Turner standard
   b. Using a rubber bulb pipet, fill the "LS Vial" with the low Turner standard
   c. Using a rubber bulb pipet, fill the "QCS Vial" with the Working QCS standard you prepared above.
   d. Use the 90% Acetone squeeze bottle to fill the "BLK Vial".

2. The Fluorometer display will go dark after a few minutes. Touch the screen to turn it back on.

3. From the Fluorometer display screen, proceed as follows:

   a. Press "Chl-NA"
   b. Press "OK"
   c. Press "Calibrate"
   d. Press "Run New Calibration"
   e. Press "ug/l"
   f. Insert the BLK Vial, press OK
   g. Wait for the Standards Display to appear
   h. Insert the LS Vial
   i. From the keyboard, enter the LS value, then press OK
   j. Press OK
   k. Press "Enter More Standards"
   l. Wait for Standards Display to appear
   m. Insert the HS Vial
   n. From the keyboard, enter the HS value, then press OK
   o. Press OK
   p. Press "Proceed With Current Calibration"
   q. Press "No" for save calibration
   r. Press "Measure Fluorescence Temp"
   s. For the Volume of Water display, press 1, then OK
   t. For the Volume of Solvent display, press 1, then OK
   u. Record the result (should be ± 10% of the true HS value) beside the High Standard "Found Value" on the Quality Control sheet.

v. Remove the HS Vial and insert the LS Vial.
w. Press "Measure Fluorescence Temp"
x. For the Volume of Water display, press 1, then OK
y. For the Volume of Solvent display, press 1, then OK
z. Record the result (should be + 10% of the true LS value) beside the Low Standard "Found Value" on the Quality Control sheet.
aa. Remove the LS Vial and insert the QCS Working Standard Vial
bb. Press "Measure Fluorescence Temp"
cc. For the Volume of Water display, press 1, then OK
dd. For the Volume of Solvent display, press 1, then OK
ee. Record the result in Table 3 beside "Fluorometer QCS Calibration".

4. Referring to Table 3, transfer the Spectrometer calibration calculation to the block marked "Spectrometer Calibration". Calcualte the % RPD between the Flurometer QCS Calibration and the Spectrometer Calibration. The acceptance criteria for this difference is $\pm$ 15%.

C. Sample Analysis:

1. One at a time, proceed as follows for each sample extract:

a. **Carefully** remove the first group of tubes from the centrifuge and place them in a plastic rack.

b. Beginning with the LRB tubes, carefully transfer some of the clear extract from each tube to a screw cap vial using a rubber bulb pipet.

c. Clean the vial with paper toweling and place inside the sample holder of the Fluorometer.

d. Press "Measure Fluorescence Temp".

e. For the "Volume of water", enter the amount in milliliters from "Sample Amount Used" from the Bench Sheet (normally 1000 mls for the various LRB's and 150 mls for the samples).

f. For the "Volume of Solvent", enter the amount in milliliters from "90% Acetone Solvent Amount" from the Bench Sheet (normally 25 ml).

g. Record the LRB results in the appropriate place on the bench sheet, and on the Quality Control sheet.

h. Analyze the five opening QC standards and record the values on the Quality Control sheet.

i. Analyze samples 1-10 plus the first duplicate, following steps b-g above. Record the values on the Bench Sheet. Duplicate acceptance limit is 10% (RPD).

j. Analyze the CCS High Standard and the CCB (90% Acetone) and record the values on the Quality Control sheet. The CCS result should be + 10% of the true value. The CCB result should be<0.5 ug/l

k. Analyze samples 11-20 plus the second duplicate, following steps b-g above. Record the values on the Bench Sheet. Duplicate acceptance limit is 10% (RPD).

l. Analyze the CCS High Standard and the CCB (90% Acetone) and record the values on the Quality Control sheet. The CCS result should be + 10% of the true value. The CCB result should be<0.5 ug/l.

m. Repeat the procedures outlined in paragraphs k. and l. above for remaining groups of 10 samples or less.

Revision/Review Date: 06/02/14

COLOR, APPARENT
STANDARD METHODS 2120B-2001

(This method can be found in "Standard Methods for the Analysis of Water and Wastewater", 21st Edition, 2001 Revision.)

1) Record all sample information on a raw data sheet. Analyze pH and record on raw data sheet. If pH is not between 4 to 10 units adjust with either hydrochloric acid or sodium hydroxide to approximately 7 pH units and note the adjustment.

2) Pour samples to the 50 ml. mark in a nessler tube.

3) Prepare any standards needed to bracket the samples if they are not already prepared. (Write down all standards you use to bracket the samples.)

4) Visually compare sample with color standards. This is done by looking vertically downward through the tubes toward a white surface. View the tubes at an angle so the light can reflect through the tube.

5) Record value to nearest color standard.

6) If the value exceeds 100 color units dilute the sample with distilled water volumetrically until it is within range.

7) If sample is "less than" the 5.0 unit standard then record the result as <5.

Calculation

$$CU = \frac{\text{Color value x 50}}{\text{mls. of sample}}$$

Report as: "Apparent Color"

Standards

Platinum-Cobalt Standard. Dilutions are made as follows with de-ionized water directly in the nessler tubes:

0.5 mls. to 50 mls. = 5.0 units
1.0 mls. to 50 mls. = 10.0 units (and so on)

Make new standards every 6 months.

Quality Control
-Analyze a duplicate every 10 samples. Re-analyze if values are not within 5 units of each other.
-Check expiration date on standards with each use.
-Holding time is 48 hours at 4C.

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Page 1 of 1

Revision/Review Date: 12/09/13

TOTAL SUSPENDED RESIDUE (TSR)

STANDARD METHODS 2540D-1997

(This procedure can be found in "Standard Methods", 21st Ed, 1997)

1) Prepare filter pads by pre-washing with 3-20 ml. portions of DI water. **Dry filter pads at 103-105C for 2 hours.** Place in dessicator and allow to cool completely. Leave in dessicator for at least 1 hour or longer until pads are at room temperature.

2) Weigh prepared filter pad to the 4th decimal place on the analytical Balance and record weight on raw data form. Record all required sample Information on raw data form. Include a filter pad blank at the beginning of each sample run. Analyze a duplicate every 20 and one at the end of each sample run.

3) Place weighed filter pad on filter apparatus and seat with DI water. **SHAKE SAMPLE VIGOROUSLY.** Using 100 ml. graduates (or 500 ml. graduates on very clear samples) filter as much sample as possible up to 1 liter followed by 3-10ml. rinse portions of DI water. Make sure each rinse portion filters through before the starting the next rinse portion. Continue suction for about 3 minutes after filtration is complete. If less than 20 mls. is used re-analyze sample using a pipet to measure sample while stirring on a mixer. If less than 5 mls. is used make a dilution such as 5 mls. to 500 mls. with DI water. Make sure to include the dilution factor in the final answer. **Use sufficient sample to obtain between 2.5 mg and 200 mg of residue per pad.** Record the amount of sample filtered on the raw data form.

4) Place the wet filter pad on the proper numbered planchet on the stainless steel tray. Place the tray in the drying oven. Record date and time placed in oven on raw data sheet.

5) Leave samples in the oven for at least 2 hours (overnight if possible)at 103-105 C. Remove the trays and place in a dessicator. Record date,time removed from oven, and oven temperature on raw data sheet. Record oven temperature in log book.

6) Leave in dessicator for at least 1 hour or longer until pads are at room temperature. Weigh pads to the 4th decimal place on the analytical balance. Record results on raw data sheet.

Calculation: $\text{TSR, mg/l} = \frac{(\text{weight2} - \text{weight1}) \times 1{,}000{,}000}{\text{mls. sample}}$

LOWER REPORTING VALUE: 2.5 mg/l (If using 1000 mls. of sample)
Adjust "less than" value accordingly if less than 1000 mls. sample was used and there was less than 2.5 mg of residue on the pad after drying

Supplies

Filter Pads. Millipore Cat.# **AP40 047 05 or equivalent**

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Page 1 of 2

TSR Page 2 of 2

Quality Control

- Analyze a filter pad blank daily.
- Analyze a duplicate every 20 samples. Duplicates which have a weight difference of <0.0025 g for both samples is recorded as 0.0% difference. Take corrective action if not within established QC criteria.
- Analyze a quality control known quarterly and record in log book.
- Holding time: 7 days, 4C.
- Record oven temperature in log book.
- Do not pour sample that will not filter back in to the graduate. Either ad an additional weighed Filter, process the remaining sample, and add the two filter weights and amounts filtered together or start with a new weighed pad and filter less sample taken from the original sample bottle.
- Annually run a drying study.