

NATIONAL PARK SERVICE
Mississippi State University

FUNDING PACKAGE

**Department of the Interior
National Park Service
STATEMENT OF WORK
Gulf Coast Cooperative Ecosystem Studies Unit
COOPERATIVE AGREEMENT NO. H5000 02 0271**

TITLE: Level 1 Water Quality Inventory Natchez Trace Parkway

Principal Investigator:

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Total: Not to exceed \$54,450

Fiscal Year Funding: Fiscal 2007

Submitting Date: June 4, 2007

END DATE: December 31, 2008

I. SCOPE OF WORK

BACKGROUND

In 1998 the National Parks Omnibus Act authorized and directed the Secretary of the Interior to “enter into cooperative agreements with colleges and universities, including but not limited to land grant schools, in partnership with other federal and state agencies to establish cooperative study units to conduct multi-disciplinary research ...” In response, a national network of Cooperative Ecological Studies Units (CESU) was developed.

The Gulf Coast CESU is one of seventeen partnerships established nationally by CESU Coordinating Council in Washington, DC to facilitate research, technical assistance and educational experiences in support of the National Park Service (NPS) and its partners.

The partnership brings together multiple federal agencies, academic institutions and non-government organizations from a distinct biogeographic area, the Gulf Coast, to address management needs in an interdisciplinary, ecosystem-oriented context. The Institute of Renewable Natural Resources of Texas A&M University (College Station, TX) serves as the institutional lead for the program. Dr. Robert Shaw, is the Associate Gulf Coast CESU Coordinator for the host university.

Objectives:

Statement of Work:

1. Project Justification

For a park not known, at least in the circles of NPS hydrologists, there is a considerable amount of quality water resources along the Natchez Trace Parkway (NATR). From the bedrock streams of Tennessee, through the loess banks of northern Mississippi, and onto the cypress sloughs and swamps of the lower Trace, water is ubiquitous. The 740 kilometers of the parkway crosses eight watersheds: the Cumberland, Duck, Buffalo, Tennessee, Tombigbee, Yockanookany, Pearl, the Big Black rivers, and several smaller watersheds (classified by the state as "South Independent Streams" in southwestern Mississippi). While the vast majority of streams are crossed without access or even signage, there are dozens that provide an interpretative backdrop, both cultural and natural, and recreational stops to cool a summer traveler. There are also scores of streams, largely hidden from the motorist, that are exemplary in biological diversity and those that have achieved non-attainment status relative to water quality.

It is reasonable to assume that a parkway that is 740 km long and bisects over 30 significant streams (order 2 or higher), that land use upstream from each stream crossing will be manifested in water quality where it crosses the parkway. The vast majority of the parkway winds through the rural south. Watersheds are dominated by agrarian and sylvan land uses. The parkway does pass through two urban areas; Tupelo and Jackson Mississippi. Several small streams are partially drained by these municipalities, albeit, mainly residential in land use.

Human recreational contact is prevalent in streams, especially so in the high-gradient, bedrock and gravel channels of Tennessee and Alabama. Recreation diminishes southward as sluggish streams and banks are bedded in mud and silt. A typical summer weekend sees nearly every visitor access point situated along a waterbody full of vehicles and their associated streams full of visitors. Although each state may classify recreational contact with different language, we can generally apply both primary-contact (swimming and wading), and secondary-contact (fishing and other non-emersion activities) at most streams of the parkway.

A review of species lists indicates the presence of three federally (threatened) listed fish: bayou darter (*Etheostoma rubrum*), slackwater darter (*Etheostoma boschungii*) and spotfin chub (*Cyprinella monacha*). Five mussels are also federally listed as endangered: orange-nacre mucket (*Lampsilis perovalis*) birdwing pearly (*Conradilla caelata*), orange-footed pearly (*Plethobasus cooperianus*), pale lilliput pearly (*Toxolasma cylindrellus*),

and the tan riffle shell (*Epioblasma walkeri*). The American alligator (*Alligator mississippiensis*), federally threatened, is also listed for the Parkway. State listings include the fish; crown darter (*Etheostoma corona*), crystal darter (*Crystallaria asprella*) and flame chub (*Hemitremia flammea*), and the aquatic amphibians; hellbender (*Cryptobranchus alleganensis*) and northern spring salamander (*Gyrinophilus prophyriticus*).

In light of the many streams of the NATR, with significant aquatic biological life and recreational opportunities, very little is known relative to the quality of its waters. Many streams have no record of water quality. Other streams where water quality data have been gathered are typified by a few scattered samples taken under different protocols.

2. Project Objectives

The objective of this project is to complete a water quality inventory of 45 streams within the Natchez Parkway in accordance to Gulf Coast Network (GULN) water quality sampling protocols. Information gained through this study will allow the GULN to focus its long-term water quality monitoring program at the parkway.

II. APPLICABLE DOCUMENTS

H5000 02 -0271 Cooperative Agreement Gulf Coast CESU

UNIVERSITY AGREEMENT NUMBER (if other than TAMU):

III. TASKS

Essentially there is one main task in this agreement: quarterly water sample collection, field measurement, and laboratory analysis at 45 locations within NATR. This task can be further detailed as follows:

- The Cooperator will begin sampling and complete the first round of site visits during the autumn quarter of 2007.
- The Cooperator will sample each site every three months over a 12 month period – to produce a “quarterly” record of water quality. These quarterly samples will be taken, one each of the four seasons, at times that represent typical seasonal flow conditions.
- The Cooperator will sample 45 sites (Appendix A) within the Natchez Trace Parkway four times over the course of one year – beginning after finalization of this Scope of Work. Any changes in sample locations will be discussed with COTR. Water samples will be analyzed for the parameters listed on Appendix B.
- Water quality sampling and analyses will be conducted under existing Gulf Coast Network water quality monitoring protocols and standard operating procedures (Appendix C); these shall be known as the “Project Protocols”.
- Laboratory analysis will be completed in accordance to *Standard Methods for the Examination of Water and Wastewater* or by analytical methods approved by the USEPA.
- It is the responsibility of the Cooperator to assure that all field members designated to collect, describe, or transport water samples, including field measurements, are trained in these tasks to the project protocols.

- Either one sample, or 10% of one daily sampling effort (which ever is less) will be collected as a duplicate as a QA/QC sample. Collection and analysis will be done in accordance to project protocols.
- The Cooperator will notify the GULN Hydrologist (CORT) if any field or laboratory parameters are found in violation of designated use standards within one day of result determination.
- The Cooperator will provide the following laboratory information for each parameter:
 - Method number
 - Sample holding times
 - Method Detection Limits (MDL)
 - Practical Quantitation Limits (PQL)
 - Lower Quantification Limit
 - Upper Quantification Limit

IV. SUBSTANTIAL INVOLVEMENT

A cooperative agreement requires collaboration between the cooperator and the National Park Service. The project addresses the mission of the Gulf Coast CESU and fulfills the criteria of substantial involvement as follows:

The University agrees to:

1. Accomplish all objectives and tasks listed in the Statement of Work.
2. Provide all materials not supplied by the NPS.
3. Participate in an oral and/or verbal dialogue with the COTR throughout the duration of this project, relating inventory activities, findings, and problems.

The National Park Service agrees to:

1. Provide location data of the 45 water sampling sites.
2. Provide all necessary permits.
3. Provide general project oversight and logistical assistance.

V. PRODUCTS AND SCHEDULE

The cooperator shall deliver to the NPS COTR, one hard (paper) copy and one copy of all documents in digital format (Microsoft Word) of all products. Final payment contingent upon receiving final report from PI.

Water quality sampling will occur during each of the four seasonal quarters: fall, winter, spring and summer. The PI will choose the actual sampling dates based upon flow conditions that typify each season. Samples may be taken during October-November (fall), January-February (winter), April-May (spring), and July-August (summer). It is anticipated that the first round of quarterly sampling will occur during the fall of 2007 (unless conditions and timing allow a summer sample to be taken in 2007). At the latest, the summer sample will be taken during July-August 2008, which will conclude the fourth and final sample round.

The PI will deliver water quality data: which includes a brief trip report, field data, and laboratory data within one week of acquisition to the COTR. The trip report will be

submitted as a Word file to the CORT. Water quality data will be delivered in the NPStoret Excel data delivery format – provided by the NPS. These deliverables are to be submitted after each quarterly round is completed. Water quality data include all parameters found in Appendix B.

The PI will deliver to the CORT a brief project report (Word), digital images (JPG) of sampling sites and any other data collected during this project by December 31, 2008.

BUDGET

Funding and Budget:

Personnel	20,686
Sample Analysis	20,997
Travel	4,657
<i>Total Direct Costs</i>	<i>46,340</i>
GCCESU 17.5% overhead	8,110
TOTAL	54,450

Budget Justification and Explanation:

Sample Analysis includes quarterly analysis of 45 samples, plus an additional 10% of total as part of the QA/QC program, during the course of the project for the parameters listed in Appendix B.

Travel includes lodging, per diem and vehicle mileage.

Budget Summary for additional fiscal years if applicable:

N/A

V. KEY PERSONNEL

NATIONAL PARK SERVICE

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TEXAS A&M UNIVERSITY

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CONTRACTING CONTACT (and full address) for PI Institution:

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ATTACHMENT 4.10

COOPERATIVE AGREEMENT INTERNAL CHECKLIST

PRE-AWARD			
	YES	NO	COMMENTS
1. Do all key officials responsible for initiating and administering Cooperative Agreements have a copy of the <i>National Park Service Agreements Handbook</i> ?	X		Handbook is readily available on the internet.
2. Does the Contracting Officer and/or solicitor agree that this should be a Cooperative Agreement in lieu of a contract? Is solicitor review documented in the file?	X		Solicitor has reviewed Cooperative Agreement Number: H5000 02 0271.
3. Will competitive procedures be followed in the award of this agreement? If action is non-competitive, is there adequate justification in the file, including the appropriate statutory authority to support the non-competitive action?	X		Non-Competitive Award. Task Order to Cooperative Agreement H5000 02 0271 [Texas A & M Univ.].
4. Do all key officials have access to 43 CFR 12, appropriate OMB Circulars, and other regulations, and understand their duties with regard to the Cooperative Agreement process?	X		Items are available in the regional office and/or on the internet.
5. Do key officials who will be administering the agreement have the required 24-hours of training?			X—COTR will address contracting issues. Gulf Coast Inventory and Monitoring network will oversee the project and have assigned the COTR
6. Is this agreement written in accordance with the handbook?	X		
7. Has an appropriate PR been received with certification from a program official that funds are available for the project?	X		SERO generated the purchase request and certified by the Contracting Officer.
8. Have the recipient's past performance and eligibility for assistance been considered in the award process?	X		

9. Is the recipient's financial management system adequate to maintain required fiscal records?	X		
10. Are the recipient's requirements, if any, for Government-furnished property addressed in the initial agreement?	X		SOW indicates any government-owned property will be housed. at the department and inventoried annually.
PRE-AWARD <i>continued</i>			
	YES	NO	COMMENTS
11. Is recipient's property management system adequate to maintain required accountability records?	X		
12. Has the agreement been reviewed and approved by the solicitor's office? Is solicitor review documented in the file?	X		The initial Cooperative Agreement has been reviewed by the solicitor's office.
13. Are agreement files accessible and do they contain all necessary documentation?	X		Original Documents are retained by the NPS Contracting Officer. Copies of relevant documents are retained by the GC-CESU Program Coordinator. The University maintains administrative budgeting and provides monthly invoices.
14. Has obligation and copy of agreement been sent to AOC? (Use Agreement Information Sheet, Attachment 4.14).	X		Region has forwarded necessary documents to SER Contracting Officer (C. Richardson). Two universities are involved so two sets of this project have been submitted (GCCESU and SACESU)

/s/

Gillian Bowser
GC-CESU Coordinator

Date July 25, 2007

July 25, 2007

MEMORANDUM

FROM: Dr. Gillian Bowser /s/
Coordinator, Gulf Coast CESU

TO: Cheryl Richardson
Contracting Officer, SERO

SUBJECT: Project Suitability Review for GC-CESU Cooperative Agreement H5000
02 0271

A review of the project, *Natchez Trace Water Quality* has been completed. An evaluation of the statement of work and proposal (technical and cost) have been completed by the CESU Coordinator, Gillian Bowser. The technical aspects of the project and the costs were judged to be acceptable for the tasks detailed in the statement of work.

The suitability of this project for a task agreement for modification of the cooperative agreement [**Agreement Number: H5000 02 0271**] was also reviewed and found to be acceptable for use of this funding instrument. Attachments 4.8 and 4.10 of Directors Order 20 [Documentation for use of a Cooperative Agreement and The Cooperative Agreement Internal Checklist, respectively] has been completed to the best of my ability and are attached to this document for inclusion in your files. The following represents the findings of the project review of suitability for modification of the cooperative agreement:

CONTRIBUTION OF PROJECT TO OBJECTIVES OF THE CESU:

SUBSTANTIAL INVOLVEMENT BY EACH PARTY: Check the appropriate types of substantial involvement used in this project

- Agency and recipient collaboration or joint participation in reviewing and modifying proposals, data, and or reports. Dr. Dibble has worked cooperatively with a variety of parks within the CESU and is well respected.
- Agency and recipient joint supervision of faculty assigned to project.
- Substantial, direct agency involvement is anticipated prior to activity to insure compliance with environmental protection (NEPA) as well as in obtaining necessary permits.
- Substantial collaboration to incorporate findings into park operations.

Please feel free to contact me [979 845-9787; gbowser@tamu.edu] if you have additional questions or comments regarding this project and the request to modify this cooperative agreement.

ATTACHMENT 4.8

Cooperative Agreement Number: H5000 02 0271.

Project: *Natches Trace Water Quality*

PI: Dibble

DOCUMENTATION FOR USE OF A COOPERATIVE AGREEMENT

A.1. What type of competition is appropriate?

Under the CESU agreement, the Gulf Coast Inventory and Monitoring network (GULN) solicited interest in this project among partner universities

A.2. Why was this cooperator selected?

This cooperator has a well established record of working with GULN and its member parks and is a local specialist in the field.

B.1. Explain the nature of the anticipated substantial involvement.

Dr. Dibble works closely with GULN staff and the hydrologist on the water quality assessments.

B.2. Why is the substantial involvement considered to be necessary?

The university is a member of the Gulf Coast CESU and because they have completed several successful projects with parks, the park staff work closely with the cooperator.

C.1. Explain why the project or activity entails a relationship of assistance rather than a contract.

See Above

C.2. What is the public purpose of support or stimulation?

Water quality is an important issue for the Natches Trace and this project also involves several endangered and threatened species.

C.3. Which law or laws authorize granting of assistance for performance of this project or activity?

Legislation is specific to establishment of a Cooperative Agreement and of the CESUs.

D.1. How was the determination made that the costs proposed are accurate and proper?

The cooperator worked with GULN to determine appropriate costs

Approved:

/s/

Gillian Bowser
Key Official

Date

Cheryl Richardson
Contracting Officer

Date

*D .1. is for non-competitive agreements only.

Appendix A

Water Quality Inventory Sites

RED: Non-attainment (303d list)

BLUE: Biological Interest

GREEN: Park Management Interest

Site	MM	State	Latitude (NAD83)	Longitude (NAD83)	Rare fish	Biologic interest	303D	Rec. Use	WQ Parameters
Dobbins Branch	430	TN	35 54 22.7	87 00 25.9	No	Yes	No	No	Temperature pH, SpC, DO, Nutrients
Garrison Creek	428	TN	35 52 31.9	87 01 50.1	No	No	No	Yes	Temperature pH, SpC, DO, Bacteria
Burns Branch	425	TN	35 50 53.7	87 03 11.9	No	Yes	No	Yes	Temperature pH, SpC, DO, Nutrients, Bacteria
Duck River (Gordon House)	408	TN			No	Yes	No	No	Temperature pH, SpC, DO, Nutrients
Jackson Falls	405	TN	35 41 48.4	87 17 45.9	No	No	No	Yes	Temperature pH, SpC, DO, Bacteria
Fall Hollow	393	TN	35 35 01.3	87 25 44.6	No	No	No	Yes	Temperature pH, SpC, DO, Bacteria
Little Swan Creek	385	TN	35 31 47.0	87 27 12.8	No	No	No	Yes	Temperature pH, SpC, DO, Bacteria
Buffalo River, Metal Ford	383	TN	35 27 48.6	87 28 47.3	No	Yes	No	Yes	Temperature pH, SpC, DO, Bacteria
Chief Creek	382	TN			No	No	No	No	Temperature pH, SpC, DO
Jack's Branch	378	TN	35 24 49.6	87 30 58.4	No	No	No	Yes	Temperature pH, SpC, DO, Bacteria

Site	MM	State	Latitude (NAD83)	Longitude (NAD83)	Rare fish	Biologic interest	303D	Rec. Use	WQ Parameters
Glenrock Branch	364	TN	35 15 16.3	87 30 58.4	No	Yes	No	Yes	Temperature pH, SpC, DO, Nutrients, Bacteria
Sweetwater Branch	363	TN	35 15 03.0	87 39 06.5	No	Yes	No	Yes	Temperature pH, SpC, DO, Nutrients, Bacteria
Cypress Creek	344	TN	35 01 51.3	87 49 19.2	Yes	Yes	No	Yes	Temperature pH, SpC, DO, Nutrients, Bacteria
Cooper Branch	341	TN	35 00 26.6	87 49 17.0	Yes	Yes	No	No	Temperature pH, SpC, DO, Nutrients
Lindsey Creek	337	Al	34 56 30.8	87 49 43.0	Yes	Yes	No	No	Temperature pH, SpC, DO, Nutrients
Burcham Branch	335	AL	34 55 29.1	87 50 36.7	Yes	Yes	No	No	Temperature pH, SpC, DO, Nutrients
Colbert Creek (Rock Spring)	331	AL	34 51 25.9	87 54 17.6	No	Yes	No	Yes	Temperature pH, SpC, DO, Nutrients, Bacteria
Buzzard Roost Spring	320	AL	34 45 35.5	88 01 24.5	No	No	No	No	Temperature pH, SpC, DO
Bear Creek	313	AL	34 40 23.0	88 05 20.9	No	No	No	Yes	Temperature pH, SpC, DO, Bacteria
Cedar Creek	310	AL	34 38 40.6	88 07 48.7	No	Yes	No	No	Temperature pH, SpC, DO, Nutrients
Tishomingo Creek (SP)	305	MS			No	No	No	Yes	Temperature pH, SpC, DO, Bacteria

Site	MM	State	Latitude (NAD83)	Longitude (NAD83)	Rare fish	Biologic interest	303D	Rec. Use	WQ Parameters
Jourdan Creek	296	MS	34 31 00.9	88 1 29.4	No	Yes	No	No	Temperature pH, SpC, DO, ANC, Nutrients
Rock Creek	295	MS	34 30 29.2	88 18 07.7	No	Yes	No	No	Temperature pH, SpC, DO, ANC, Nutrients
Twentymile Creek	278	MS			No	No	Yes	No	Temperature pH, SpC, DO, ANC, Nutrients
Mud Creek	268	MS			No	No	Yes	No	Temperature pH, SpC, DO, ANC, Nutrients
Town Creek	267	MS			No	No	Yes	No	Temperature pH, SpC, DO, ANC, Nutrients
Chuquatonchee Creek	241	MS			No	No	Yes	No	Temperature pH, SpC, DO, ANC, Nutrients
Houlka Creek	231	MS			No	No	Yes	No	Temperature pH, SpC, DO, ANC, Nutrients
Old Field Creek	217	MS	33 41 16.0	89 02 30.3	No	Yes	No	No	Temperature pH, SpC, DO, ANC, Nutrients
Line Creek	213	MS	33 39 12.7	89 04 19.5	No	Yes	No	No	Temperature pH, SpC, DO, ANC, Nutrients
Big Bywy Ditch	196	MS			No	No	Yes	No	Temperature pH, SpC, DO, ANC, Nutrients
McCurtain Creek	186	MS	33 21 28.0	89 20 08.3	No	Yes	No	No	Temperature pH, SpC, DO, ANC, Nutrients

Site	MM	State	Latitude (NAD83)	Longitude (NAD83)	Rare fish	Biologic interest	303D	Rec. Use	WQ Parameters
Cole Creek	175	MS	33 13 44.1	89 26 45.7	No	Yes	No	No	Temperature pH, SpC, DO, ANC, Nutrients
Hurricane Creek	165	MS	33 04 59.0	89 31 30.1	No	Yes	No	No	Temperature pH, SpC, DO, ANC, Nutrients
Ninemile Creek	141	MS	32 47 01.8	89 41 21.4	No	Yes	No	No	Temperature pH, SpC, DO, ANC, Nutrients
Fourteen Mile Creek	71	MS			No	No	Yes	No	Temperature pH, SpC, DO, ANC, Nutrients
Fivemile Creek	65	MS	32 10 15.3	90 39 36.6	No	Yes	No	No	Temperature pH, SpC, DO, ANC, Nutrients
Big Sand Creek	59	MS	32 07 01.3	90 45 59.3	No	Yes	No	No	Temperature pH, SpC, DO, ANC, Nutrients
Little Sand Creek	55	MS	32 05 28.4	90 47 53.4	No	No	No	Yes	Temperature pH, SpC, DO, ANC
Bayou Pierre	45	MS			No	Yes	No	Yes	Temperature pH, SpC, DO, ANC, Nutrients
Little Bayou Pierre	40	MS			No	No	Yes	No	Temperature pH, SpC, DO, ANC, Nutrients
North Fork Coles Creek	24	MS	31 46 47.9	91 08 26.1	No	No	Yes	No	Temperature pH, SpC, DO, ANC, Nutrients
Mud Island Creek	22	MS	31 46 00.1	91 09 50.5	No	Yes	No	Yes	Temperature pH, SpC, DO, ANC, Nutrients
South Fork Coles Creek	17	MS			No	No	Yes	No	Temperature pH, SpC, DO, ANC, Nutrients

Appendix B

Water Quality Inventory Parameters

Field Data

Site ID code*	NNNN
Sample Collection Date	DD/MM/YYYY
Sample Collection Time	24:00 (CST)
Weather Condition Code**	X
Days since last significant rainfall	DD
Air Temperature	(°C)
Specific Conductance	(µS)
Dissolved Oxygen	(mg/l)
Dissolved Oxygen	(% saturation)
Water Temperature	(°C)
pH	(SU)
Turbidity	(NTU)
Flow Condition Code***	X

Laboratory Data

Nitrate	(mg/l)
Nitrite	(mg/l)
Total Nitrogen	(mg/l)
Phosphate	(mg/l)
Total Phosphorous	(mg/l)
Sulfate	(mg/l)
Ammonium	(mg/l)
Potassium	(mg/l)
Magnesium	(mg/l)
Calcium	(mg/l)
Total Suspended Solids	(mg/l)
Acid Neutralizing Capacity	(mg/l)
<i>Escherichia coli</i>	(colonies/100ml)

*Site ID Code will be provided by CORT

**Weather will be recorded by standard “World Meteorological Observation” classes listed below:

- 0 Cloudless.
- 1 Cloudy or partly cloudy.
- 2 Overcast.
- 3 Drifting snow, or dust/sand storm. Visibility < 1000 M.
- 4 Fog or dust. Visibility < 1000 M.
- 5 Drizzle or light rain.
- 6 Rain.
- 7 Snow, sleet, or hail.
- 8 Rain showers.
- 9 Thunderstorms. Squalls. Rain, sleet, snow, or hail.

*** Flow Condition will be recorded as one of the following options:

Dry

Low

Normal

Flood

Above Normal

No Flow

Interstitial Flow

Appendix C

Applicable GULN Water Quality Sampling Protocols

Water Quality Monitoring Protocols for the Inland Parks of the Gulf Coast Network

Standard Operating Procedure (SOP) # 1

Training of Field Personnel

Version 1.0 (December 2006)

Revision History Log:

Prev. Version #	Revision Date	Author	Changes Made	Reason for Change	New Version #

Field personnel may be stationed at VICK, NATR and GULN and CUPN offices. It is of utmost importance that each sampler has a fundamental knowledge of hydrology and field practices to assure the quality of data collected. Basic knowledge includes safety concerns, location and access of sample stations, operation and calibration of equipment, sample extraction, preservation, and shipment techniques.

It is anticipated that during the many years of program operation several individuals will be involved with sample collection. To assure that there is a seamless transition between one sampler and the next the following SOP will be used.

Each new sampler will spend at a minimum of one day per park with the CUPN-GULN Hydrologist, the designated trainer. Prior to field activities, all aspects of the pre-sampling checklist will be reviewed. Over the course of the day, routes and access to each site will be discussed, with special care to safety aspects (flood flow, snow and ice, vehicle traffic, venomous snakes, etc).

During the first station visit the trainer will perform all sampling activities, explaining in detail, all aspects of collecting high-quality samples; including equipment operation, precise sample extraction location and technique, field book notation, and noteworthy hydrologic observations. At each point in the sampling activities, the trainer will explain

to the trainee where things can go wrong. The first site visit typically takes about twice as long as a normal visit as every aspect of sampling is reviewed.

As the training day progresses, the trainer permits the trainee to perform sampling duties, beginning with sample extraction, and progressing through in situ measurement and field observations. After the trainee has demonstrated the ability to perform all aspects of sampling, the trainer will allow the trainee to fully sample a station while standing in observation. By the end of the day, the trainer, after taking the trainee to a station, will “disappear”, allowing the trainee to be on their own for the site visit. After all activities are completed, the trainee will summon the trainer for review. If all duties are completed to the satisfaction of the trainer, the trainee is considered to possess the basic competencies for water quality sampling.

Training Checklist

Calibration of probes	
Safety issues	
Route finding	
Sample extraction	
QA-QC measures and sample extraction	
Field book notation	
In situ measurement	
Field analysis	
Sample preservation	
Sample transportation	
Data transmission	

Water Quality Monitoring Protocols for the Inland Parks of the Gulf Coast Network

Standard Operating Procedure (SOP) # 2

Pre-Sampling

Version 1.0 (December 2006)

Revision History Log:

Prev. Version #	Revision Date	Author	Changes Made	Reason for Change	New Version #

Successful water quality sampling involves the use of many devices and gear. It is extremely frustrating for the sampler to arrive at a remote station only to find out that a battery is dead, a sample bottle was left behind, or a notebook is misplaced. In order to eliminate lost time and perhaps lost samples, a simple pre-event checklist is provided. The sampler should not simply peruse the list the morning before the sampling event. The sampler must check the list, especially for supplies, a week before sampling in case additional supplies are needed, and again the night before the event for last-minute details (such as charging batteries, warming incubators, etc). Finally, as the sampler prepares for the field, the list should be checked once again to assure nothing is being left behind. As simple as it sounds, being well-prepared prior to sampling may be the difference in lost data and repeated efforts.

PRE-EVENT WATER QUALITY SAMPLING CHECK-LIST

- Cooler with ice
- Backpack (to contain sampling gear and supplies)
- Sample bottles
- pH/SPC combination meter and backup
- pH calibration buffers
- SPC calibration solution
- DO meter and backup
- 8 spare *AAA* cells
- 4 spare *D* cells
- Marsh-McBirney Flo-Mate 2000
- Wading staff
- Tape
- Tape pins/clips
- Field book/pen/pencil/marker
- Scientific calculator
- Distilled water
- Distilled water squirt or spray bottle
- Bacteria sample bottles
- Instrument log book
- NIST-traceable thermometer
- Waders (if needed)
- Emergency First-Aid kit
- Small tool kit
- Flashlight
- Barometer watch
- Sampling gloves

Water Quality Monitoring Protocols for the Inland Parks of the Gulf Coast Network

Standard Operating Procedure (SOP) # 3

Collection of Field Data

Version 1.0 (December 2006)

Revision History Log:

Prev. Version #	Revision Date	Author	Changes Made	Reason for Change	New Version #

Details of each sampling event are recorded in a field book. Field books are prepared on pre-printed “rite-in-rain” notebooks and a new page is used for each station. These data may provide useful insights to water quality interpretation. As the sampler arrives in the field, a page will be dedicated to the following general information (*italics are entry examples*). Each station will be completed for the following information. Be sure that all data are recorded in the correct units. The field data sheet will be arranged as follows:

Weather will be recorded by standard “World Meteorological Observation” classes listed below:

WMO 4501 Weather Condition Code List

0	Cloudless.
1	Cloudy or partly cloudy.
2	Overcast.
3	Drifting snow, or dust/sand storm. Visibility < 1000 M.
4	Fog or dust. Visibility < 1000 M.
5	Drizzle or light rain.
6	Rain.
7	Snow, sleet, or hail.
8	Rain showers.
9	Thunderstorms. Squalls. Rain, sleet, snow, or hail.

- Discharge will be calculated in the database upon returning from the field and entered into the field database as L/s.
- “Flow Condition” is based on NPStoret field.
- Some parks will rely on a laboratory for determining fecal coliform concentrations, others will perform fecal coliform filtrations in the field. After incubating at 44.5 °C for 24 hours, the samples will be counted and entered into the field database.
- Discharge calculations are provided to the samplers in a MSEXcel datasheet.

- For pre-sampling calibration, record calibration results (three standards for pH, one for SpC).
- For post-sampling calibration check, record instrument value when placed into specific standard solutions.
- Maintenance indicates any changes to sensor (including cleaning, replacement) as well as battery changes, etc.

**Water Quality Monitoring Protocols for the
Inland Parks of the Gulf Coast Network**

Standard Operating Procedure (SOP) # 4

Field Measures

Version 1.0 (December 2006)

Revision History Log:

Prev. Version #	Revision Date	Author	Changes Made	Reason for Change	New Version #

Comparison of water quality trends over time relies not only on quality observations and sample collection procedures of the samplers, but also on standardized equipment and standardized measurement practices. This SOP, which in large part was adapted from “Water Quality Inventory Protocol: Riverine Environments” (Stednick and Gilbert, 1998).

Water Temperature

- Definition:** Thermal content of a solution on an absolute scale
- Container:** In-situ determination
- Volume Required:** Not applicable
- Preservation:** Not applicable
- Holding Time:** Not applicable
- Field Procedure:**

Water temperature is important because it may indicate thermal pollution and influences most physical, chemical, and biological processes. Gas-diffusion rates, chemical-reaction rates, and the settling velocity of particles are just a few of the many processes related to

water temperature. In addition, temperature differences between water sources and seasonal variations in temperature make temperature useful in hydrologic investigations, particularly those that involve the mixing of groundwater and surface water.

For economy and ease of use, the liquid-in-glass thermometer is recommended for field use. A pocket-sized thermometer protected by a plastic or metal case is recommended. Mercury filled thermometers should be avoided since breakage may occur in the stream and the spilled mercury may be toxic. To eliminate the problem of column separation, it is best to use a thermometer with gas-filled capillary.

Most thermometers shipped from the manufacturer are not highly accurate. Before each new thermometer is issued for field use, it should be checked for accuracy. This is done by comparing the field thermometer to a precise instrument such as an ASTM calibration thermometer at three points. The comparison is usually made in a water bath to eliminate erratic readings. Any thermometer found to be off by more than 0.5°C should be rejected.

Temperature measurements should be made directly in the stream if possible. The following steps should be taken when making temperature measurements:

1. Check thermometer for liquid-column separation.
2. Immerse bulb into source.
3. Allow the reading to stabilize.
4. Read temperature with bulb immersed (removing the bulb from water can result in an erroneous temperature reading due to rapid thermometer response to changing conditions).
5. If temperature cannot be measured in the source, collect (at a minimum) an 8-ounce (500 ml) bottle or beaker of water and measure the temperature immediately. Shield the sample from the sun and wind while measuring.
6. Return thermometer to protective case.

Note: Temperature of the sample is required for accurate calibration of the instrumentation for dissolved oxygen, pH and conductivity. Temperatures should be recorded with results of these analyses. Air temperatures can be collected on-site, and provide useful information for site characterization as well.

Analytical Method: ASTM E1-58: Standard Specifications for ASTM Thermometers
APHA 2550: Temperature
STORET No : 00010, Temperature, water (Degrees Celsius)

Precision: ± 0.5 °C

Reporting: Report to nearest 0.5 °C

pH

Definition: The pH value is the negative base-10 logarithm of the hydrogen ion (H^+) activity in the water. Values may range from pH 1 to pH 14, with pH 7 neutral, less than 7 acidic and greater than 7 basic. Each pH unit represents a tenfold change in H^+ activity. pH is important in the toxicity and solubility of many constituents, for example, ammonia.

Container: Field determination (Polyethylene or teflon beaker)

Preservation: Refrigeration to 4°C

Holding Time: 6 hours

Field Procedure:

Because the pH of some samples can change in a short time, it should be measured in the field with a reliable pH meter.

Electrometric: The pH meter used in conjunction with a glass electrode and reference electrode (or a combination glass plus reference electrode) develops a voltage potential in response to the hydrogen-ion activity without interference from most other ions. This method of measurement has become the standard for accurately determining pH in the field and laboratory.

It is important that maintenance and calibration be provided for all pH meters. If the pH meter is properly maintained and calibrated, field values may be more valid than lab values due to changes in pH with time and temperature fluctuation.

Calibration: Calibrate meter and electrode according to manufacturer's instructions using three buffer solutions (for example 4, 7 and 10). To avoid contamination of buffers, calibration and meter checks should be conducted in buffer solution in separate containers, such as small disposable paper cups. Buffer solutions should be discarded after use. Often in parks only occasional pH measurements are made, therefore it is critical to calibrate the instrument before each measurement. When frequent measurements are made, the meter calibration should be checked at least twice a day. If the meter is drifting appreciably it will need to be recalibrated more frequently - or it may need new electrodes. If in-situ measurement is not possible, a water sample should be collected and analyzed immediately for pH. This sample is then discarded.

Measurement of Sample pH

1. Place electrode into sample (split sample that is discarded after measurement).
2. Measure temperature.
3. Turn function switch to "measure" or equivalent

4. Allow meter readout to stabilize (this may take several minutes if the solution is poorly buffered).
5. Record pH to nearest 0.1 pH unit.
6. Cover electrode with protective cap of electrode storage solution.

Precautions

- Never remove electrode from buffer or sample unless meter is in "standby" or "off" position. To do so may polarize the electrodes, permanently damaging them and resulting in unstable meter readings.

- Dirty connectors on pH electrodes may result in erroneous readings; do not handle the plug; if it is dirty, clean it with ethanol or isopropyl alcohol.

- The GULN typically uses gel-filled electrodes which require no internal solution maintenance. If, however, liquid-filled electrodes are used, keep electrode filled with the recommended solution to within 1/2 inch of filling opening. Do not substitute a filling solution of different chemical composition made for another electrode. Keep the fill hole closed when the electrode is not in use to prevent evaporation of the filling solution. It is suggested that gel-filled electrodes be used to avoid electrolyte problems.

- Keep electrode tip moist by filling the provided rubber cap with either pH 7 buffer solution, electrode storage solution, or de-ionized water. If the tip dries out, soak it in pH 7 buffer solution for 24 hours. Even when using "dry-storage" electrodes, keep electrode in storage solution when not in use to assure rapid response and long electrode life.

- Never immerse the electrode to such a depth that the surface of the filling solution is below that of the test solution. Again, gel-filled electrodes eliminate this problem.

- The temperature compensator on most meters must be set for the temperature of the sample that is being measured; however, on several brands of inexpensive meters the "temperature" compensation knob is also used as a "slope" knob to calibrate the meter to the second buffer. The GULN program will use automatic temperature compensation meters.

-When these meters are used the buffers must be at the same temperature as the water being sampled. This can be accomplished by immersing the container of buffer in the stream being sampled until the temperatures are similar.

- Do not let the electrodes freeze.
- Avoid contamination of buffer.
- Broken or scratched electrodes can give erroneous readings.
- Do not leave meter exposed to extreme weather conditions.

Note: Change in temperature will affect the ionic equilibrium of the solution resulting in an alteration of the pH measurement. Effort should be made to calibrate the instrument using buffer solutions within 5° C of the sample. The pH meter should include temperature compensation mechanism to minimize temperature effects on the electrode.

Analytical Method: ASTM D1293-84 : Standard Test Methods for pH of Water
APHA 4500-H⁺ : pH Value
STORET No : 00406: pH, field [Standard Units = SU]
Electrometric - glass electrode in combination with reference potential (typical: saturated calomel) electrode.
pH measurement of waters of low conductivities: ASTM D5128-90.

Precision: ± 0.1 Standard Unit (of pH)
Reporting: Report to 0.1 Standard Unit

Specific Conductance

Definition: The ability of a solution to carry an electric current. Conductivity can be used as an approximation of the dissolved solid content of the solution. Reported in microSiemens (μS).

Container: in-situ determination

Volume Required: not applicable

Preservation: not applicable

Holding Time: not applicable

Field Procedure:

Specific conductance is useful in estimating the concentration of dissolved solids in water. Rather precise field measurements of specific conductance can be made with a specific conductance meter. Most conductance meters are an adaptation of the Wheatstone resistor bridge with built-in circuitry capable of converting resistance values (ohms) to conductivity values (mhos). Most natural waters have a conductivity of much less than 1 S (Siemens are the same as mhos, the former will be used as a conductivity reporting unit for the GULN), and to avoid decimals, values are usually reported in microSiemens - the observed value in Siemens times 1,000,000.

Specific conductance is dependent upon water temperature, and by convention, values are adjusted to 25°C (standard temperature and pressure). Basically all modern conductivity instruments have a temperature compensation mechanism that automatically adjusts readings to the 25 degree standard. The GULN will use only temperature compensated sensors.

It also is advisable to check a field instrument's automatic calibration mechanism periodically. This may be done by warming and cooling a single water sample in the laboratory, above and below 25 degrees, and observing the instrument's ability to correct its reading back to the 25-degree value. In most solutions an increase of 1°C will increase conductance by approximately 2 percent.

Specific conductance electrodes should be rinsed occasionally in a hydrogen peroxide solution or a weak acid solution (5 percent) to prevent debris and algae from accumulating. Maintenance and calibration of conductance meters should follow manufacturer's instructions.

Calibration and Measurement of Specific Conductance

The GULN will use automatic temperature compensated meters for all specific conductance measurements.

1. Check battery
2. Calibrate as per manufacture's instructions using a traceable standard of 447 $\mu\text{S}/\text{m}$ or 10 μS , whichever is closer to the conductivity of sample waters.
3. Read conductance according to manufacturer's instructions.
4. Record sample measurement
5. Remove probe from sample and rinse thoroughly with de-ionized or distilled water.

Precautions

- Gently agitate electrode in sample to eliminate air bubbles.
- Allow water temperature and electrode temperature to equalize.
- Make sure electrode is clean.
- Do not leave meter exposed to extreme weather conditions.

Analytical Method: ASTM D1125-91 : Standard Test Methods for Electrical Conductivity and Resistivity of Water
APHA 2510 : Conductivity
STORET No : 00095: Specific conductance (micromhos/cm @ 25⁰ C) Electrometric

Precision: Standard deviation not to exceed 5% of measured value (National Handbook of Recommended methods for Water-Data Acquisition)

Reporting: Record specific conductance in mS/m at 25°C to two significant figures. Examples: Measured value of 1926 is reported as 1900; measured value of 48.6 is reported as 49.

Dissolved Oxygen

Definition: Dissolved oxygen (DO) is a measure of the amount of oxygen in solution. Oxygen solubility is controlled by solution temperature and the partial pressure of oxygen within gasses in contact with the solution. Adequate DO is necessary to maintain diverse aquatic communities and fisheries. Dissolved oxygen is influenced by photosynthetic and microbiologic activity and can be subject to significant daily variation. Water quality monitoring programs that include DO should consider these influences.

Container: in-situ determination

Volume Required: not applicable

Preservation: not applicable - immediate analysis

Holding Time: not applicable - immediate analysis

Field Procedure

Dissolved oxygen (DO) should be measured in-situ or in the field, as concentrations may show a large change in a short time if the sample is not adequately preserved. Dissolved oxygen concentrations may be determined directly with a DO meter. DO instrument calibrations are usually done in units of % saturation and should be performed on site. A station pressure (i.e. barometric pressure uncorrected to sea level) in millimeters of mercury (mm Hg) may be obtained from a built-in barometer to the instrument display, from a hand-held barometer or the nearest weather station. Alternatively, the instrument may permit dialing in an altitude to correct for barometric pressure change as in most instances, corrections for altitude may be all that is necessary. Currently GULN samplers are equipped with wrist barometers capable of resolving absolute pressure to one mm Hg.

Dissolved Oxygen Meters

Dissolved oxygen meters can be used to measure dissolved oxygen concentrations in-situ, in the field. The GULN will use galvanic cell DO meters. The procedure is as follows:

1. Calibrate the instrument as per manufacture's instructions. Meters currently used by the GULN are easily calibrated in water-saturated air. Make sure that the current barometric pressure (uncorrected, absolute pressure) is entered into the meter setup menu. Recalibration and pressure entry should be done prior to a DO measurement at each monitoring site.
2. Place the probe in the solution to be measured and agitate the probe. Let the probe come to temperature and measurement stabilize before recording values.

3. If measurements are in waters with low turbulence, gently stir the probe in the water, without inducing aeration.

Report both the concentration (mg/L) and the percent saturation (%) for each sample. This is done as the saturation (partial pressure) of any dissolved gas in a liquid is dependent on the temperature of the liquid.

Analytical Method: ASTM D888-92 : Standard Test Methods for Dissolved Oxygen in Water

APHA 4500 - O : Oxygen Dissolved

STORET No: 00299: Oxygen, dissolved, analysis by probe [mg/L]

Precision: ± 0.05 mg/L DO (APHA)

Reporting: Report to nearest 0.1 mg/L DO, and to the nearest 0.1%

Acid Neutralizing Capacity

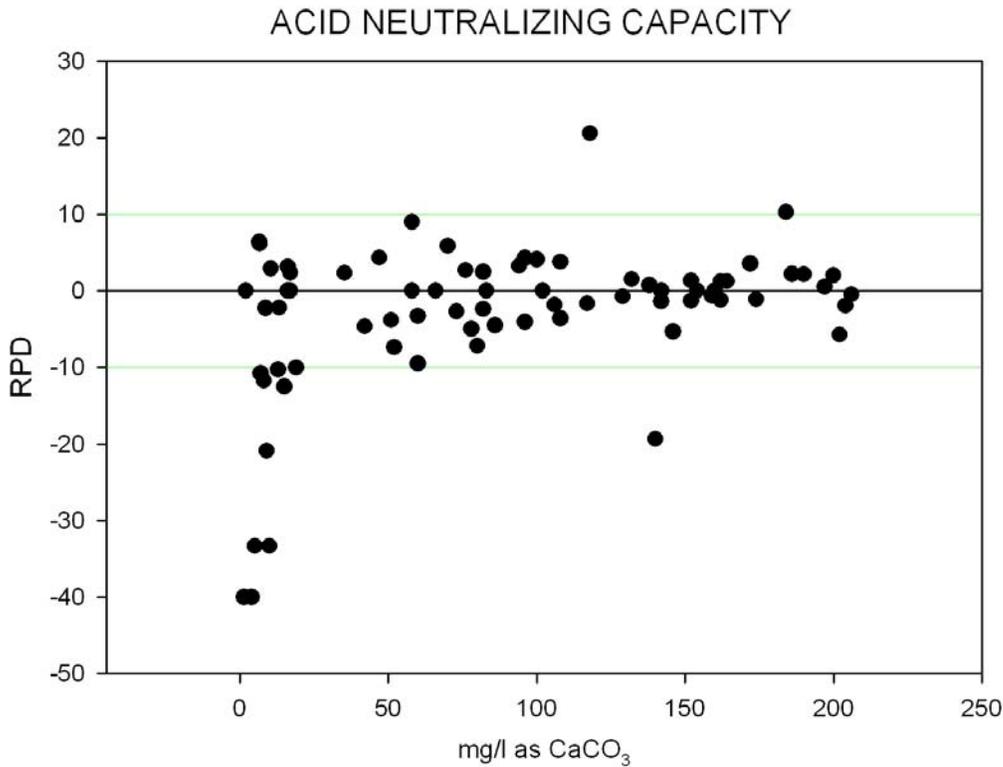
Definition:	Capacity of a water to neutralize an acid to a specified pH endpoint. ANC differs from alkalinity since the pH equivalence point is determined analytically rather than fixed (i.e. pH 4.5) in order to more accurately describe the capacity of a water to neutralize the H ⁺ ion. GULN field procedure will use the Gran titration.
Container:	HDPE or glass
Volume Required:	100 ml
Preservation:	ice
Holding Time:	12 hours
Field Procedure:	ANC determinations will be made the classic Gran titration. Protocol developed by the CUPN (as follows) will be used.

Acid Neutralizing Capacity Protocol for the Cumberland Piedmont Network
 Joe Meiman, Mammoth Cave National Park; March 2005

Alkalinity and ANC are at times used interchangeably. They are both a measure of the sum of all titratable bases, however alkalinity samples are filtered (0.45 µm) to account for only dissolved phase ions while ANC is not filtered and is considered a total account.

ANC is of particular interest in that it is a measure of how well a body of water can buffer the effects of acids. Soluble acids occur naturally, from humic and fulvic acids associated with the decay of plant material, carbonic acid naturally occurring in precipitation, as well as anthropogenic acids emitted to or created in the atmosphere from human-related sources – commonly referred to as acid rain. We have demonstrated that many of the CUPN parks, especially so in the Piedmont, have very low ANC values, in the range of 1 to 20 mg/l as CaCO₃. It is in these waters which warrant long-term monitoring of ANC.

Upon review of water quality data collected during the first two years of our program it became apparent that the Hach Alkalinity field titrations were not accurate enough in the low range, especially below 10 mg/l as CaCO₃. The following graph of relative percent differences (RPD) between a sample and its duplicate shows that the Acid Neutralizing Capacity (ANC) method began to deteriorate at levels below about 15 mg/l as CaCO₃.



To alleviate this problem, the CUPN Science Technical Committee (January 14, 2005) suggested either developing a new protocol for ANC, or modifying an existing method. As the soundness of any program relies upon using approved methods, the best course of action was to slightly modify an existing approved method, Standard Method 403 Alkalinity. The major modification to this method consists of incorporating use of an electronic micro-burette in place of the previously-used standard micro-burette. The electronic micro-burette is capable of resolving titrant volumes to the nearest 0.01 ml, while the standard glass micro-burette is generally graduated in 0.05 ml increments. The real and practical advantages are higher titration precision along with ease and safety of use in a field environment. It is difficult, at best, to perform Gran titrations in the field with a glass micro-burette. The new delivery system of the electronic micro-burette is fully enclosed and easily portable from one site to another.

The following is a transcription of Standard Methods for the Examination of Water and Wastewater, 16th Edition, Method 403 Alkalinity. Any modifications to this method⁷ which will only be for the use of the electronic micro-burette or for special things the analysis should be aware of, will be noted by *italics*. This method has special considerations for low-range alkalinity, concentrations lower than 20 mg/l as CaCO₃, and they will be used in this transcription. Fourteen lab trials were made by the author using this exact method. Split sample runs of three solutions (ranging from 50, 20, and 16 mg/l as CaCO₃ were made. The former solutions comprised four trials, while the latter included six trials. Standard deviations were approximately 1% (or less) of the average value (see attached table for trial details).

1. General Discussion

- a. Principle: Hydroxyl ions present in a sample as a result of dissociation or hydrolysis of solutes react with the additions of standard acid. Alkalinity thus depends of the end-point pH used. For methods of determining the inflection points from titration curves and the rationale for titrating to fixed end-points, see Section 402. 1a.

For samples of low alkalinity (less than 20 mg/l as CaCO₃) use an extrapolation technique based on the near proportionality of concentration of hydrogen ions to excess of titrant beyond the equivalence point. The amount of standard acid required to reduce pH exactly 0.30 pH unit is measured carefully. Because this change in pH corresponds to an exact doubling of the hydrogen ion concentration, a simple extrapolation can be made to the equivalence point.

- b. End-Points: When alkalinity is due entirely to carbonate or bicarbonate content, the pH at the equivalence point of the titration is determined by the concentration of carbon dioxide (CO₂) at that stage. CO₂ concentration depends, in turn, on the total carbonate species originally present and any losses that may have occurred during titration. *The remaining portion of this discussion is for phenolphthalein alkalinity,*

where end-points are determined by color change (the same process as used in the Hach titrations).

- c. Interferences: Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause sluggish response. Allow additional time between titrant additions to let electrode come to equilibrium or clean the electrodes occasionally. Do not filter, dilute, concentrate, or alter sample.
- d. Selection of Method: *Since this method is specifically for low alkalinity waters, it will be assumed that only the low alkalinity method will be used and discussed below. If the analyst would prefer to use this method for all alkalinity titrations, please follow the guidelines found in Method 403.*
- e. Sample Size: For the low alkalinity method, titrate a 200 ml sample with 0.02 N H₂SO₄ from an *electronic* micro-burette.

2. Apparatus:

- a. *Electronic micro-burette, capable of controlling drops of titrant to 0.02 ml.*
- b. Magnetic stirrer.
- c. Stir bar (approximately 1 cm).
- d. 250 ml beaker.
- e. 200 ml volumetric flask.
- f. 5 ml pipette.
- g. Calibrated pH meter, capable of resolving pH to +/- 0.01 SU.
- h. Bottle (upon to mount the electronic micro-burette) of 0.02 N H₂SO₄.
- i. Rinse bottle of De-ionized water.

3. Reagents:

Note: The following reagents will be mixed at the MACA office and shipped to CUPN water quality samplers. The sodium carbonate solution is used to determine the normality of the standard acid (not shipped to the field), while the standard acid, with its measured normality, will be shipped to the samplers.

- a. Sodium carbonate solution, approximately 0.05 N: Dry 3 to 5 g primary standard Na₂CO₃ at 250°C for 4 h and cool in a desiccator. Weigh 2.5 +/- 0.2 g (to the nearest mg), transfer to a 1 L volumetric flask, fill flask to the mark with distilled water, dissolve and mix reagent. Do not keep longer than 1 week.
- b. Standard sulfuric acid: Prepare acid solution of 0.02 N H₂SO₄ as indicated under Preparation of Desk Reagents. Standardize against 40.00 ml of 0.05 N Na₂CO₃ solution, with about 60 ml of water in a beaker by titrating potentiometrically to a pH of about 5. Lift out electrodes, rinse into the same beaker, and boil gently for 3 to 5 min under a watch glass cover.

Cool to room temperature, rinse the cover glass into beaker, and finish titrating to the inflection point. Calculate the normality:

$$\text{Normality, } N = A \times B / (53.00 \times C)$$

Where:

A = g Na₂CO₃ weighed into 1 L flask,
 B = ml Na₂CO₃ solution taken for titration,
 C = ml acid used.

Use measured normality in calculations or adjust to 0.1000*N*; 1 ml 0.1000 *N* solution = 5.00 mg CaCO₃.

- c. Standard sulfuric acid, 0.02 *N*: Dilute 200.00 ml 0.1000 *N* standard acid to 1000 ml with distilled water. Standardize by potentiometric titration of 15.00 ml of 0.05 *N* Na₂CO₃ according to the procedure of 3b; 1 ml = 1.00 mg CaCO₃.

4. Procedure

- a. Potentiometric titration to pre-selected pH: Prepare sample and titration apparatus. Titrate to an end-point of 4.9 SU without recording intermediate pH values and without undue delay. As the end-point is approached make smaller additions and be sure that pH equilibrium is reached before adding more titrant.
- b. Potentiometric titration of low alkalinity: For alkalinities less than 20 mg/l titrate 100 to 200 ml according to 4a, above using an electronic microburette and 0.02 *N* standard H₂SO₄. Stop the titration at a pH in the range 4.3 to 4.7 and record volume and exact pH. Carefully add additional titrant to reduce the pH exactly 0.3 pH units and again record volume.

5. Calculation for low alkalinity water

Total alkalinity, mg CaCO₃/L

$$= (2B-C) \times N \times 50,000/\text{ml sample}$$

Where:

B = ml titrant to first recorded pH,
 C = total ml titrant to reach pH 0.3 unit lower, and
 N = normality of acid

Helpful Tips

These tips, although not found in the above method are good advice for analysts new to Gran titrations.

- Make sure the pH meter is very responsive and great care is taken in calibration. You will find that as the end-point is approached, a sluggish probe will cause problems in accurately attaining a solid end-point.
- Use a volumetric flask to measure the sample. Since we are dealing with very low values, accurate measures of all reagents and sample is critical.
- Place the pH electrode in the beaker at an angle, with the bulb end resting where the side and bottom meet and the top end resting on the opposite rim. This will permit water to circulate across the probe and keep the probe from the stir bar.
- Operate the magnetic stirrer at the lowest speed possible to avoid any streaming potential that could impact pH measurements. The stirrer speed should be just enough to adequately mix the water.
- Before titrating, get used to the electronic micro-burette. This is a new device and quite simple to use, but a bit of practice is recommended.
- Do not operate the pump too fast. A steady turn of the crank is all that is needed. If the crank is turned too fast, air bubbles can be introduced to the delivery line. Keep an eye on the line to make sure no bubbles are present during titration.

The apparatus set up is represented in the following image:



Note the pH probe is resting on the rim of the beaker and positioned off-center as to not be interfered with the stir bar. The electronic micro-burette is to the right screwed to the top of a shatter-proof bottle containing the standard acid.

trial	sample vol	mp vol	mp pH	ep vol	ep pH	ANC	stndev
1a	100	5.65	4.33	5.83	4.04	54.7	
2a	100	5.57	4.51	5.72	4.22	54.2	
3a	100	5.5	4.61	5.66	4.32	53.4	
4a	100	5.47	4.66	5.65	4.34	52.9	0.804156
1b	100	2.82	4.49	2.94	4.2	27	
2b	100	2.79	4.68	2.92	4.37	26.6	
3b	100	2.86	4.63	2.99	4.34	27.3	
4b	100	2.79	4.65	2.9	4.36	26.8	0.298608
1c*	100	1.96	4.69	2.06	4.38	18.6	
2c	100	1.8	4.69	1.91	4.37	16.9	
3c	100	1.83	4.6	1.94	4.31	17.2	
4c	100	1.84	4.49	1.97	4.19	17.1	
5c	200	3.68	4.46	3.97	4.15	16.95	
6c	200	3.57	4.61	3.77	4.32	16.85	0.666083 0.145774

* air bubble in deliver line. The first SD calc (0.67) of this trial includes this point, the second SD calc (0.15) in does not

all volumes are in ml

ANC result is mg/l as CaCO₃

mp is the midpoint (inflection point) of the titration

ep is the end point of the titration

Analytical Method: Gran titration, CUPN from Standard Methods for the Examination of Water and Wastewater, 16th Edition, Method 403 Alkalinity
STORET Number: 02320: Alkalinity, field titration

Precision: see above

Reporting: Report as mg/l CaCO₃

Stream Discharge Measurement

Stream discharge is defined as the unit volume of water passing a given point on a stream or river over a given time. Stream discharge is typically expressed in cubic feet per second (cfs) or cubic meters per second (cms) and is based on the continuity equation or velocity-area method $Q = A * V$, where A is the cross sectional area of the stream at the measurement point and V is the average velocity of water at that point. All GULN discharge data will be ultimately calculated and reported as liters per second (l/s).

Streamflow at any point in time is an integration of the streamflow generation and routing mechanisms in a watershed at that time. This integration also defines the water quality at that time, including land use activities, point source discharges and natural sources. Thus streamflow measurement should be considered an essential component of water quality monitoring. Streamflow measurements are useful for water quality data comparisons over time, interpretation of water quality data, and calculation of parameter loads. Streamflow measurements will be made at each water quality location at the time of each water quality sampling.

Equipment List for Stream Discharge Measurement

1. Flow meter. The GULN will use Marsh-McBirney Flomate 2000.
2. Tape measure - cloth tape is recommended.
3. Stakes - end stakes for anchoring tape measure to stream banks.
4. Pencil.
5. Field book.

Site Selection

Each sampling site was chosen prior to sampling. The exact position to make the discharge profile may vary over time as the stream characteristics may change following flood events. However, the discharge measurement must be made proximal (within 50 m) of the water sampling location and may not have any flow additions or subtractions (tributaries, diversions) between the discharge profile and the sample extraction location.

1. Immediate stream reach - reasonably straight, narrow, free of rapids, pools, islands, and eddies; uniform, laminar flow.
2. Obstructions - free of large rocks, bottom debris, algae, weeds, and hanging plants from banks.
3. Bed material - avoid mud, large cobbles, and boulders.

Site Preparation

1. If necessary, move small obstructions and debris (before measurement only).
2. Set tape measure and stakes perpendicular to flow.
3. Calculate number and size of intervals; recommend no more than 10 percent of flow in any one interval or 5 percent for large rivers.
4. Find edge of water by looking straight down on the tape measure.

Field Measurement

The velocity measurements are made in the stream while wading when the depth and velocity of water permit safe crossing of the stream. The individual taking depth and velocity measurements will stand downstream of the measurement point and in a position that least affects the velocity of the water passing the current meter (obtained by standing behind the meter facing upstream). The wading rod is held at the tape in a vertical position with the meter parallel to the direction of flow while the velocity is being observed. The field procedure for determining flow by velocity is outlined in the following steps:

1. A tape will be suspended across the channel perpendicular to the direction of flow to measure the top width of flow.
2. Suitable stream width increments to make velocity measurements will be determined.
3. The flow rate at each increment is measured using a top setting wading rod.
4. The velocity measurements will be taken by setting the current meter on the wading rod to the proper depth.
5. Repeat velocity measurement at each incremented cross-section.
6. The measurements will be taken at equal intervals across the stream. A minimum of five measurements will be taken in the stream. For narrow streams, this may require measurements at 1 foot intervals or less. If the majority of flow is confined to one section of the stream, such as the center of the stream, the measurements should be taken at smaller increments in the majority of the flow and at larger intervals elsewhere across the stream. Usually no individual increment should contain more than ten percent of the total flow. However, it is not required that measurements always be taken at one or two foot intervals. The point at which the measurements are taken is recorded according to the distance shown on the tape line suspended across the stream. For the streams in the area, it is recommended that depth and velocity measurements be taken at one foot intervals across the stream and at smaller intervals where the flow is concentrated.

The depth of flow is measured at each increment using the wading rod, as previously outlined. The rod is placed vertically in the stream at a specific interval along the tape line so the base plate of the rod rests on the streambed. The depth of water is read on the graduated rod to the nearest 0.05 feet. As previously indicated, the person holding the wading rod should stand downstream in a position that least affects the flow at the sensor.

Several different velocity methods can be used to determine the average flow velocity at a point. Two methods that are appropriate for measuring the average velocity for the streams in the area are the six-tenths depth method or the two-point method. Selection of the specific method depends on the depth of flow. The six-tenths depth method will be the primary method for measuring average velocity and is used whenever the depth of flow is less than 2.5 feet (USGS, 1977). All sampled GULN streams will be wadable and be measured using the six-tenths method.

Data Record

Data will be recorded in the field book. The data recorded in the field includes the distance from initial point, depth, observation depth (the depth at which the velocity was measured), and velocity.

Discharge is calculated by the rational equation:

$$Q = \Sigma (VA)$$

Where: V = velocity

A = cross sectional area.

The total discharge of the stream is the sum of the discharges in the partial sections:

$$Q = q_1 + q_2 + q_3 + \dots q_n$$

Where: Q = total discharge of stream

q_1 = discharge of stream section 1

q_2 = discharge of stream section 2

q_n = discharge of last stream section.

When the sampler returns from the field, discharge data will be entered and calculated in the MSAccess discharge calculation field. It is common that conditions will exist that make a standard discharge profile impossible or unsafe, such as flood conditions. When such conditions are present, the sampler is asked to estimate discharge. Over time the sampler will become well familiar with the site and will be able to judge the cross-sectional area of flow. Once familiar with the site, the sampler may effectively estimate velocity from timing the surface velocity of debris, and thus estimate discharge. It is

imperative that the sampler makes note if the discharge value is estimated and not measured in such cases.

Total coliform and *E. coli*

Definition:	These bacteria, found in fecal matter of warm-blooded animals, are common to the waters of the GULN, as found by the water quality inventory. In many cases fecal bacteria exceed state designated use standards.
Container:	Sterile HDPE or glass
Volume Required:	100 ml (unfiltered)
Preservation:	wet ice
Holding Time:	24 hours
Lab Procedure:	Total coliform and <i>E. coli</i> determinations will be made using enzyme substrate Standard Method 9223.
Analytical Method:	Standard Method 9223 STORET Number: 11737; Total Coliform 9780; <i>E. coli</i>
Precision:	1 colony
Reporting:	colonies/100 ml

The CUPN initially used the MFC fecal coliform method. This method, although a standard for years, has various shortcomings. Relative percent differences between duplicate samples were high across the range. Samples must be plated within six hours of collection, often creating logistical problems. Individual colony counts were at times difficult, and typically exceeded the recommended number of colonies per plate. To rectify these issues we have now adapted the enzyme substrate method, SM 9223. The following MPN *E. coli* and total coliform protocol was developed following Standard Method 9223 by the CUPN.

Total Coliform and E. coli Protocol for the Cumberland Piedmont Network

Tom Diggs, Cumberland Piedmont Network, March 2006

One important aspect of the measurement of general water quality is the quantification of the presence or absence of certain species of microorganisms. These groups of organisms are typically either pathogens or serve as indicator species for the overall bacterial load a water body or stream receives. This bacterial load, if elevated, can indicate if a stream is receiving high levels of pollution which can support the growth of these microbes. The concentration of these organisms can therefore be used as a yardstick for the overall sanitary condition of a body of water.

Bacteria of the coliform group, *Escherichia coli* in particular, have long been recognized as excellent indicators for the sanitary quality of natural waters because 1) they are indicators of the amount of fecal pollution being received by waters, since they are native enteric bacteria, and 2) because they are relatively easy and reliable to culture and quantify. *E. coli*, as well as many other enteric bacteria which can be present in fecal pollution, such as fecal streptococci and enterococci, can also be dangerous and potentially lethal pathogens to both humans and native biota. Because of their pathogenicity and their ability to strongly correlate with overall water quality, it is important to be able to quantify them.

During the first two years of water quality monitoring within the Cumberland Piedmont Network, we used a membrane filter method for determination of fecal coliform concentration. We used a field-portable M-FC medium-based procedure which proved reliable, but impractical. It did not give us the ability to differentiate *E. coli* from the overall coliform picture, and it was highly subject to incidental contamination, since it relied on scientists manipulating sterile membrane filters in sometimes highly nonsterile (rain, snow, mud, insects, etc.) environments.

In October, 2005, IDEXX's Colilert procedure was adopted because of its demonstrable reliability, ability to readily differentiate *E. coli* from other coliform bacteria, and swiftness and ease of field use. This commercial procedure is included in the American Water Works Association's Standard Methods for the Examination of Water and Wastewater as protocol 9223 – Enzyme Substrate Coliform Test. The following (italicized) discussion is transcribed from the 21st edition of Standard Methods:

1. General Discussion

- a. *Total coliform bacteria: Chromogenic substrates, such as ortho-nitrophenyl- β -D-galactopyranoside (ONPG) or chlorophenol red- β -D-galactopyranoside (CPRG), are used to detect the enzyme β -D-galactosidase, which is produced by total coliform bacteria. The β -D-galactosidase enzyme hydrolyzes the substrate and produces a color change, which indicates a positive test for total coliforms at 24 h (ONPG) or 28 h (CPRG) without additional procedures. Noncoliform bacteria, such as *Aeromonas* and *Pseudomonas* species, may produce small amounts of the enzyme, but are suppressed and generally will*

not produce a positive response within the incubation time unless more than 10^4 colony-forming units/mL are present.

- b. *Escherichia coli*: A fluorogenic substrate such as 4-methyl-umbelliferyl- β -D-glucuronide (MUG) is used to detect the enzyme β -glucuronidase, which is produced by *E. coli*. The β -glucuronidase enzyme hydrolyzes the substrate and produces a fluorescent product when viewed under long-wavelength (366 nm) ultraviolet light. The presence of fluorescence indicates a positive test for *E. coli*. Some strains of *Shigella* spp. Also may produce a positive fluorescent response. Because *Shigella* spp. are overt human pathogens, this is not considered a detriment for testing the sanitary quality of water.

2. Apparatus

- a. Incubator set to $35^{\circ}\text{C} \pm 0.5^{\circ}$.
- b. Labeled sample container, 100 ml, provided by manufacturer.
- c. Colilert substrate ampoules, provided by manufacturer.
- d. Multi-well trays (Quanti-Tray/2000), provided by manufacturer.
- e. Tray sealer.
- f. Multi-well tray carrier for use with tray sealer.
- g. Quality control organisms, provided by manufacturer.
- h. Ultraviolet-viewing chamber with long-wave UV light source and eye protection. The welder's glass provided with most UV viewing chambers is adequate for protection.

3. Procedure

- a. *Taking the sample*: Obtain the sample aseptically in the labeled sample container. The label should include **date, park code, site code, the time the sample was taken, and time zone** (if the sample was taken in a time zone different from where it is being run at the lab.) Fill the container to the 100 ml mark. Take care not to touch the inside of the container or the container lid. If taking a QA/QC sample, be sure to take the normal sample and the QA sample in parallel (at the same time,) to avoid micro-scale variations in the water. Preserve the sample in ice until ready to run it in the lab. Bacterial samples must be processed and incubated within 24 hours of taking them from the source water.
- b. *Laboratory Procedure*:
 1. Carefully label QuantiTray/2000 sterile trays with sample identity.
 2. Turn on tray sealer and allow it to warm up. A green light indicates readiness.
 3. Add Colilert substrate ampoule contents to sample bottle (aseptically, taking care not to contaminate sample.) Shake vigorously until substrate is completely dissolved.
 4. Taking care not to touch the inside of the QuantiTray while handling, pour sample/substrate solution into tray.
 5. Check small wells for bubbles and tap the tray to eliminate them. Some bubbles are inevitable in the large wells, but they do not interfere with the validity of the test, and a positive result can still

be determined if this is the case. It is much more difficult to read a positive result in the small wells if there are bubbles present.

6. Place the tray in the tray carrier, and use the sealer to seal the tray.
7. Place in a $35^{\circ}\text{C} \pm 0.5^{\circ}$ incubator for 24 ± 4 hours.
8. After minimum incubation time, read the results by yellow color change (total coliform) and UV fluorescence (*E. coli*). Interpret the results using the MPN (most probable number) table provided by Idexx manufacturer.

c. *Dilution*

There may arise occasions when running a 100% dilution of the source water will yield results which are out of range of the MPN table provided by the manufacturer. Typically, these conditions follow a heavy rainfall, when increased runoff from agricultural fields, septic system field lines, water treatment overflow, etc. result in a large amount of coliform bacteria being washed into the receiving stream. Usually, in these cases, all large wells and all small wells will be yellow and/or fluorescent, if run at full dilution, resulting in an out-of-range MPN. One may compensate for this by diluting the sample with clean, aseptic de-ionized water. Multiply the resulting MPN by the inverse of the dilution factor to determine the correct number. For example, if you run a 50% dilution, multiply the resulting MPN by 2. If you run a 10% dilution, multiply by 10.

4. Result Interpretation

1. Compare the sample QuantiTray to the comparator QuantiTray provided by the manufacturer in order to determine lower limits for color change and fluorescence. In most cases, the color change and fluorescence will be much stronger than that exhibited by the comparator, but occasionally the distinction is difficult to make, especially in the small wells. In these cases, it is important to use the comparator. The comparator trays have an expiration date. After the labeled date, contact Idexx for a fresh comparator.
2. Use the MPN table provided by the manufacturer to determine the most probable number of colonies in the sample. Count the number of large wells that turned yellow (or fluoresced under UV, for *E. coli*) and compare to the number of small wells that turned yellow (or fluoresced.) The MPN will appear on the table where these two values meet.
3. Report results as colonies per 100 ml.

5. Quality Control

1. Test each new lot of substrate by inoculation with the three control bacteria provided by the manufacturer. These bacteria, in the CUPN case, are *Escherichia coli*, *Klebsiella pneumoniae*, and *Pseudomonas aeruginosa*. Also use a sterile water control. Incubate and interpret the results as above, but if the control water exhibits a color change or fluorescence, discard and use a new batch of substrate. **Conduct the**

Quality Control with care, as the quality control organisms are live, viable, pathogenic bacteria.

2. Relative Percent Difference: The CUPN strives for a relative percent difference (RPD) between a sample and its duplicate (QAQC) of no greater than 10%. This standard will be suspended for bacterial analysis for two reasons. First, the nature of the analysis does not lend itself to RPD calculations, especially in low bacteria numbers. Secondly, the primary benefit of real-time RPD testing cannot be accomplished on bacteria samples. That is, results are not known until after a 24 hour incubation, thus retesting of the sample (or aliquot) is not possible as the holding time has been exceeded.
3. Incubator Temperature: The analyst will record the temperature of the incubator prior to placing QuantiTrays, and again prior to tray removal. A NIST-traceable thermometer ($\pm 0.1^{\circ}\text{C}$) will be used. Incubator temperature must be $35^{\circ}\text{C} \pm 0.5^{\circ}$. If the incubator is found not within this range, note on datasheet and contact the network hydrologist. Likewise, in case of power-outage, estimate likely time and duration of outage and record on datasheet.
4. Total Coliform vs. *E. coli*: *E. coli* is a coliform bacteria, thus it is a subset of total coliform. The MPN of total coliform should always be greater than that of *E. coli*. It is possible, but rather improbable, that both values are equal. An *E. coli* MPN greater than total coliform indicates that an error occurred at some point of the analysis.

6. Disposal

Exposed and incubated QuantiTrays are biohazardous, and should be disposed of accordingly.

The apparatus is shown in the following image:



Shown: UV source and hood, incubator, Colilert ampoules, labeled QuantiTray, labeled sample container, MPN table, QuantiTray with yellow color change, and tray sealer.

References

Stednick, J. D. and D. M. Gilbert. 1998. Water Quality Inventory Protocol; Riverine Environments. USDI Park Service. Technical Report NPS/NRWRD/NRTR-98/177. 103 pp.

**Water Quality Monitoring Protocols for the
Inland Parks of the Gulf Coast Network**

Standard Operating Procedure (SOP) # 5

Sample Collection, Preservation, and Transportation

Version 1.0 (December 2006)

Revision History Log:

Prev. Version #	Revision Date	Author	Changes Made	Reason for Change	New Version #

Much of the following SOP narrative was adapted from “Water Quality Inventory Protocol; Riverine Environments” (Stednick and Gilbert 1998).

Sample Labeling

A sample identification scheme has been developed that includes sample station identification and type of sample analysis. This type of labeling scheme is useful as a control check, and invaluable if the field book is lost.

For example: **NATR – GCGC 191 BACT**

NATR (4-digit park code) Natchez Trace Parkway

GCGC (4-digit station code) Garrison Creek

191 (julian date)

BACT (analysis) bacteria

The sample container should be labeled with a waterproof marking pen on a pressure-sensitive label. The sample container label should contain:

1. Sample identification
2. Time (24 hour / military)
3. Date of collection
4. Name or initials of the person collecting the sample
5. Remarks

Upon completion of sampling and field-data recording, the samples should be transferred to the laboratory under appropriate conditions. Samples should be shipped in an ice chest. A chain of custody form should be filled out by the individual doing the sampling and signed by each individual accepting custody of the sample if required. If sealing tape is used, the laboratory manager responsible for the analysis must sign the chain of custody form stating that there was no tampering with the tape sealing the container.

Stream Sampling

An efficient method of collecting water samples is to use the sample container as the sampling device. Container immersion is generally used in shallow or wadable water bodies and can be used from fixed structures (e.g., bridges) or boats.

Using sample containers, water samples can be collected by the following procedure:

1. Select the appropriate sized pre-cleaned, pre-labeled sample container. All sample containers will be supplied by the laboratory. Each sampler will be trained as to the use of appropriate containers as per SOP 1. Samples should be taken in a prearranged priority so that all sample handling and preservation can take place as rapidly as possible. Sample containers, sample size, and preservation requirements for water samples are presented by parameter. Collect the sample where the water is well mixed, immediately downstream from a point of hydraulic turbulence such as a knickpoint or where streamflow appears laminar.
2. Do not walk on, or in any way disturb, the stream bottom upstream from the sampling site.
3. All sites have been pre-determined and will not change, unless per SOP 9. Do not sample streams immediately below tributaries or other significant points of inflow, unless, of course, the sample site is designated at the mouth of a confluence. Sample far enough downstream for thorough mixing to have occurred (approximately 6 - 8 stream widths downstream from confluence point should be adequate) sample both main stream and tributary just above the confluence.

4. Clear surface debris if present. Avoid water quality sampling in pools or standing water where floating solids tend to accumulate. Rinse sample containers with the water that is to be sampled three times prior to sampling.
5. Submerge the sample container below the water surface to the appropriate depth. To avoid contaminating the sample, collect samples with the mouth of the sample bottle or collection container pointed upstream. Keep hands and other potential contaminants away from the mouth of the collection container. In a well-mixed stream, collect the sample in the center of the channel using depth integrated sampling techniques, avoiding the inadvertent collection of part of the stream bottom or top-floating materials.
6. Allow the container to fill to desired volume (e.g., leave about 1% of the container's capacity to allow for addition of preservatives (if necessary) and expansion if samples are to be shipped).
7. Remove the container from the water, filter if necessary, preserve sample as required. Secure the cap tightly.
8. Not all sample containers should be filled to the same level. Sample bottles should be filled completely if the samples are to be analyzed for pesticides and carbon. Full bottles must be protected from freezing. When sampling for bacteria, turbidity, or suspended solids, it is desirable to leave an airspace in the sample container to facilitate mixing before sub-sampling in the laboratory.
9. Rinse the container's outside surface with clean water and dry with a paper towel. Verify the sample label is correct and complete.
10. Preserve the sample as required and place the labeled sample container in an appropriate carrying container. Complete chain-of-custody documents if required and record them in the field logbook.
11. Maintain an up-to-date field book as per SOP 3.
12. Collect QA/QC samples when required (once per sampling round).
13. Rinse sampling and analytical equipment before leaving each sampling location.
14. Move to next sampling location and repeat procedures.

Springs and Very Shallow Streams

Unless pools are present, samples cannot be dipped in the normal way from springs, seeps, and very shallow streams. Water may be collected with a syringe from shallow water as long as it does not draw particulate matter from the bottom. It may be necessary to excavate a small pool or depression in order to collect adequate water volume for the sample. After disturbing the stream bed in any way it will be necessary to allow the flowing stream to clear of sediment and turbidity prior to sampling.

Field Quality Assurance

General Measures

- (a) All equipment and instruments should always be kept clean and in good working condition by means of the techniques and practices given elsewhere in this manual.
- (b) Records should be kept of all repairs to the instruments and of any irregular incidents or experiences which may affect operation.
- (c) Conditions should be such that they encourage and maintain a safe work environment, both in the laboratory and field settings.
- (d) It is essential that standardized and approved methodologies, such as those recommended in this manual, be used by field personnel. If any changes to the approved methods are made, they should be documented and experimental data obtained to ensure that the results are valid and comparable to the earlier data. No deviations of the SOPs or this narrative will be made by the sampler without prior approval of the GULN Hydrologist.

Specific Measures

The following discussion on field instruments and quality assurance was adopted from the USGS Techniques for Water-Resources Investigations (USGS, 1975).

All data measured in the field or at the duty station must be entered into the field or instrument log book. Field data includes information that may not be entered into NPStoret, but may provide additional data for future uses of the archive. Such information may include sensor performance, battery changes, and general information.

Field personnel must be familiar with all aspects of this document and associated SOPs relevant to their sampling activities. To ensure data quality:

- Calibration is required at the field site for most instruments. Make field measurements only with calibrated instruments.
- Each field instrument must have a permanent log book documenting calibrations and repairs. Review the log book before leaving for the field. (See SOP 3 for sample log book).
- Test each instrument before leaving for the field. Tests should indicate that the sensor is performing well and battery life is sufficient for the day.
- Practice your measurement technique if the instrument or protocol is new to you.
- Have backup instruments, extra sensors, and batteries readily available. Since many parks of the GULN are distal from duty stations, it is vital to check instrument performance and to carry backup supplies before leaving.

Standard Field Sampling Procedure

Before taking field measurements, allow sensor to equilibrate to the temperature of the water being sampled. Before recording field measurements, allow the measurement readings to stabilize. The criteria for stabilized field readings are defined in the table below, for a set of three or more sequential measurements. The natural variability inherent in surface waters at the time of sampling reflects the accuracy that should be attainable with a calibrated instrument.

Allow at least 60 seconds (unless otherwise specified by the manufacturer) for sensors to equilibrate with sample water. Take instrument readings until the stabilization criteria of the table below are met. Record the median of the final three or more readings as the value to be reported for that measurement point.

Standard direct field measurement	Stabilization criteria for measurements (variability should be within the value shown)
Temperature (thermistor)	+/- 0.2°C
SpC	
when $\leq 100 \mu\text{S/cm}$	+/- 5%
when $> 100 \mu\text{S/cm}$	+/- 3%
pH (meter display to 0.01 SU)	+/- 0.1 SU
Dissolved Oxygen (galvanic method)	+/- 0.3 mg/l

Prevention of Sample Contamination

The quality of data generated in a laboratory depends primarily on the quality of the samples received at the laboratory. Consequently, the field investigator must take the following precautions to protect samples from both contamination and deterioration. It should be kept in mind that there are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination during sampling include metallic or metal-containing sampling equipment, containers, lab ware, reagents, and de-ionized water; improperly cleaned and stored equipment; atmospheric inputs such as dirt and dust from automobile exhaust, cigarette smoke, nearby roads, and wires. Human contact can contaminate the samples. For example, dental work (e.g., mercury amalgam fillings) can contaminate samples exposed to exhalation (U.S. EPA, 1996-d). The following are some of the basics. More details are documented for many of the methods, such as in the new EPA 1600 Series of methods for water (U.S. EPA, 1996-d). (The list is adapted from Environment Canada, 1983).

- (a) Field measurements should always be made on a separate sub-sample, which is then discarded once the field measurements have been made. They should never be made on the same water sample which is returned to the laboratory for chemical analysis.

- (b) Sample bottles, new or used, must be cleaned according to recommended methods.
- (c) Only the recommended type of sample bottle for each parameter should be used.
- (d) Water sample bottles should be employed for water samples only. Bottles that have been used for other purposes cannot be used.
- (e) Recommended preservation methods must be used. All preservatives must be of analytical grade and included as field blanks for identification of potential contamination.
- (f) When preserving samples, the possibility of adding the wrong preservative to a sample or cross-contaminating the preservative stocks should be minimized by preserving all the samples for a particular group of parameters together.
- (g) The inner portion of sample bottles and caps should not be touched with bare hands, gloves, mitts, etc.
- (h) Sample bottles must be kept in a clean environment, away from dust, dirt, fumes and grime. Vehicle cleanliness is an important factor in eliminating potential contamination of samples and equipment.
- (i) Petroleum products (gasoline, oil, exhaust fumes) are prime sources of contamination. Exhaust fumes and cigarette smoke can contaminate samples with lead and other heavy metals. Air conditioning units are also a source of trace metal contamination.
- (j) Filter units and related apparatus must be kept clean, using procedures such as acid washes and soaking in special solutions, and should be protected from field contamination.
- (k) Bottles or sample bags which have been sterilized must remain sterile until the sample is collected.
- (l) All foreign and especially metal objects must be kept out of contact with acids and water samples.
- (m) Specific conductance should never be measured in sample water that was first used for pH measurements. Probes (such as pH probes) should be inserted into split samples to be discarded rather than into samples to be analyzed.
- (n) Samples must never be permitted to stand in the sun. Samples should be stored in the upright position at 4°C in a cool place, ice chest or equivalent.
- (o) Samples should be shipped to the laboratory without delay.
- (p) The sample collector should keep his/her hands clean while working with water samples and field equipment.

Sample Transportation

Storage Temperature - All aliquots and samples will be stored in ice chests or under refrigeration at 4°C until filtration and preservation is performed and prior to and during

delivery to the laboratory. The chlorophyll-a filter will be wrapped in aluminum foil and frozen until shipment.

The sampler is responsible for contacting either a commercial courier or the GULN office to ship samples to the laboratory. Samples will be securely packed with adequate ice packs to assure 24 hours of temperatures below 4°C. The sampler will notify the laboratory at the time of shipment to alert lab staff of the impending arrival of the samples. All chain-of-custody forms will be completed and shipped with the samples.

References

Environment Canada, 1983. Sampling for Water Quality, Water Quality Branch, Inland Waters Directorate, Ottawa.

Stednick, J. D. and D. M. Gilbert. 1998. Water Quality Inventory Protocol; Riverine Environments. USDI Park Service. Technical Report NPS/NRWRD/NRTR-98/177. 103 pp.

US Geological Survey, 1975. US Geological Survey Techniques for Water-Resources Investigations, Book 1, Chapter D1, by; Herbert H. Stevens, Jr., John F. Ficke, and George F. Smoot, 70 p.