



Cumberland Piedmont Network Water Quality Monitoring

Standard Operating Procedures

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Cumberland Piedmont Network

National Park Service
Inventory and Monitoring Division



Water Quality Monitoring Standard Operating Operating Procedure 1

Training Field Personnel—Version 1.2

Summary

This standard operating procedure (SOP) explains the steps involved in training new field personnel to conduct water-quality monitoring in the Cumberland Piedmont Network (CUPN).

Revision Log

New Version #	Date	Author	Changes Made	Reason for Change
1.1	12/9/2015	Joe Meiman	Added Tips for Successful Sampling	To improve performance of field personnel
1.2	3/3/2017	Joe Meiman	Added training component for lab work	To explicitly state lab training requirements
1.2	5/2/2017	Editor	Editorial review, format update	Protocol publication

Overview

At present, field personnel trained in the CUPN Water Quality (WQ) protocols are stationed at CUPN Headquarters (HQ), Cumberland Gap National Park (CUGA), Little River Canyon National Preserve (LIRI), Mammoth Cave National Park (MACA), and Shiloh National Military Park (SHIL). Staff members collecting samples must have a fundamental knowledge of hydrology and field practices, to ensure collection of high-quality samples and data. Basic knowledge includes safety risks and procedures, location and access to sample stations, operation and calibration of equipment, sample extraction, and sample preservation.

During the many years of program operation, several individuals will likely be involved with sample collection. This SOP is used to ensure that there is a seamless transition between one sampler and the next. Each new sampler will spend a minimum of one day per park with a trained sampler. The trainee must demonstrate competencies in SOPs 1–5 before they are considered qualified.

Proper water-quality sampling begins and ends with safety (See SOP 2—*Pre-Sampling and Safety*). No data point is worth risking one's safety. This point cannot be stressed enough as it is counter to the field instinct to "sample or bust." Prior to field activities, review all aspects of the pre-sampling checklist, including instrument calibration and safety concerns pertinent to the day's activities. It is the responsibility of the water sampler to be aware of changing field conditions that can compromise safety, and feel comfortable making the decision to suspend sampling activities if needed.

Training

Prior to any field or laboratory activities the trainee will review the protocol SOPs and the CUPN Water Quality park book. The Cumberland Piedmont Network has been collecting water-quality information since 2002, and sample conditions ranging from flood to drought have been documented. The CUPN park book (park specific) details each site, including directions, photographs, site description and expected parameter ranges. This information allows the new sampler to put the ambient condition into hydrologic context relative to flow. For example, a particular site may typically show low SpC during high flow.

During the first station visit, the trainer will perform all sampling activities. The trainer will explain 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. Over the course of the day, routes and access to each site will be discussed, with special care given to safety aspects (e.g., flood flow, snow and ice, vehicle traffic, and venomous snakes). Particular attention is given to placing the ambient condition into the range of flow conditions. 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 will permit 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 observe while the trainee fully samples a station. By the end of the day, the trainer will take the trainee to a station then “disappear,” allowing the trainee to sample 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.

Laboratory training will happen in much the same manner as field training. First, the trainer will thoroughly review any hazardous materials associated with the lab procedures including material safety data sheets (MSDS). The CUPN water sampler may be making lab determinations of ANC, nitrate, and *Escherichia coli*. The trainer will demonstrate how to successfully execute each procedure as the trainee watches. The trainee will execute subsequent tests as the trainer observes. The last test will be done with the trainer out of the room and returning to check the results.

Training Checklist:

- ☐ Review of WQ Safety Job Hazard Analysis
- ☐ Calibration of probes
- ☐ Field instrument error check
- ☐ Safety issues
- ☐ Route finding
- ☐ Field data management
- ☐ Sample extraction
- ☐ Field book notation
- ☐ In-situ measurement
- ☐ Grab sample collection
- ☐ Sample preservation
- ☐ Sample transportation
- ☐ Laboratory analysis

Helpful Hints for a Successful Water Quality Sampling Event

If the program is to succeed it must adhere to protocols and SOPs—including safety SOPs. These protocols include proper calibration and operation of field equipment, and completion of all sampling within the allotted single day. The sampler and their supervisor must both understand that water quality is the sampler’s primary duty on sampling day, except in extreme circumstances. The following tips are for the sampler:

- The day before the sample event, assemble all gear and use the checklist to account for everything.
- Prepare a field book noting the QA/QC site for the specific sampling event.
- Check that all field sensors are operational. A sampling day begins poorly if you discover while taking the first sample that your pH meter has a dead battery.

- Set up your laboratory equipment before you leave for the field. Make sure all reagents are set out and everything is ready to go when you return from the field.
- Double check the weather and be aware of changing conditions during the sample event. Do not sample or suspend sampling if safety is in question.
- Sample in the same rotation and occupy the same site at the same time of day for every event, as practical. A typical progression at Shiloh National Military Park would be:

8:30 a.m.—Owl Creek (OCOC)

9:15 a.m.—Tilghman Branch (TBTB)

9:45 a.m.—Shiloh Branch (SBSB)

10:30 a.m.—Shiloh Spring (SSSS)

11:00 a.m.—Rhea Spring (RSRS)

11:30 a.m.—Upper Dill Branch (UDDB)

12:15 p.m.—Lower Dill Branch (LDDB)

12:45 p.m.—Tennessee River at Pittsburgh Landing (PLTR)

- Proceed with laboratory analysis after lunch. Do not get side tracked. If you feel you might be distracted, have lunch after the analysis.
- Take acid neutralizing capacity (ANC) and nitrate samples from the cooler and allow to adjust to room temperature. Proceed with *E. coli* analysis. When *E. coli* analysis is complete, perform ANC analysis; when ANC is finished, complete nitrate tests.
- After completion of all laboratory analyses, clean equipment and put everything away neatly so it can be easily found the following month. Enter nitrate and ANC results in the field book.
- If any equipment is broken or not working properly, let the CUPN hydrologist know immediately. Although you have backups for all field equipment (except discharge) the CUPN hydrologist will need to get new or refurbished equipment to you well before the next event. Two days before a sample event is a very bad time to say your dissolved oxygen sensor was “acting weird” last month.
- The next day—24 hours after sealing the *E. coli* trays—count the cells.
- Complete the field book *E. coli* data.
- Write the WQ field report.
- Scan and email the data and field report to the CUPN hydrologist and data manager.
- Take an inventory of supplies. If you need anything, contact the CUPN hydrologist as soon as possible.

Cumberland Piedmont Network

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Water Quality Monitoring Standard Operating Procedure 2

Pre-Sampling and Safety—Version 1.2 Summary

This standard operating procedure (SOP) explains pre-sampling and safety procedures associated with water-quality monitoring in the Cumberland Piedmont Network (CUPN).

Revision Log

New Version #	Date	Author	Changes Made	Reason for Change
1.1	12/9/2015	Joe Meiman	Added Safety SOP	Compliance with NPS-SER safety policy
1.2	3/3/2017	Joe Meiman	Added training component for lab work	To explicitly state lab training requirements
1.2	5/2/2017	Editor	Editorial review, format update	Protocol publication

Overview

Successful water-quality sampling involves the use of many devices and assorted gear. It is extremely frustrating for the sampler to arrive at a remote station only to find they have a dead battery, a lost sample bottle, or a misplaced notebook. To eliminate lost time and data, a simple pre-event checklist is provided in this SOP. The sampler should not simply peruse the list the morning before the sampling event. Instead, the sampler must check the list—especially for supplies—at least a week before sampling, in case additional supplies are needed. The sampler should check the list again the night before the sampling event for last-minute details (such as charging batteries, and warming incubators). Finally, the sampler should check the list while preparing for the field to assure nothing is left behind. As simple as it sounds, being well prepared prior to sampling may prevent lost data and repeated efforts.

Safety

The Cumberland Piedmont Network considers the occupational health and safety of its employees, cooperators, and volunteers to be of utmost importance. The network is committed to ensuring that all field crews receive adequate training on NPS safety procedures, incident reporting, and emergency response prior to conducting field work.

Pre-Event Safety

Prior to each sampling event an email is sent to the park's natural resource contact (identified by the superintendent) describing the date of the planned activity. The sampler will send a text message to a designated CUPN contact prior to entering the field and upon completing the day's activities. The CUPN contact will have a list of sites to be visited that day and the order of the activity. Cellular coverage is generally good (carrier-dependent) in CUPN parks.

Job Safety

An important tool used to promote safe conduct is the Job Hazard Analysis (JHA; formerly called a Job Safety Analysis). The JHA approach is consistent with NPS Director's Order 50 and the *NPS Occupational Safety and Health Program: Reference Manual 50B* (NPS 2008). The JHA process is to (1) identify hazards associated with field and laboratory settings, as appropriate, and (2) develop approaches to mitigate those hazards. Prior to each water-quality sampling event, all participating field personnel must review the related JHA and agree to follow all safety guidelines during sampling. In addition to the JHA, all NPS staff must read the entire CUPN safety plan. Prior to participating in field work, all NPS staff must complete NPS Operational Leadership, first aid and CPR training.

JOB HAZARD ANALYSIS

Name of Job: Water-Quality Monitoring

Job Title: Field Crew Members

Division: I & M Cumberland Piedmont Network

Job Safety Analysis: General fieldwork; travel to, from, and within parks

Required Personnel Protective Equipment: Mode of communication (radio/cell phone/InReach/personal locator beacon), sturdy hiking boots, long pants (preferably treated with permethrin), food, water, insect repellent, first aid kit. Personal flotation device if in boat.

Recommended or Optional Equipment: Hat, long-sleeve shirt, rain gear, sunscreen, poison ivy treatment, bee sting kit (required if any crew members are allergic to insect stings), walking stick (if working in steep terrain).

Table SOP2-1. Job Hazard Analysis for monitoring of water quality in CUPN parks.

Tasks	Potential Hazards	Recommended Action or Procedure
Emergency Preparedness	Not knowing emergency procedures; Not having emergency supplies	• Know who to contact and how to reach them in the event of a life-threatening or non-life-threatening emergency. • Have current CPR and first aid certification, and know the certification status of co-workers. • Keep a well-maintained first aid kit in each vehicle and with each field team.
Hiking to/from site	Falling or tripping due to poor footing, uneven terrain, loose/rolling rocks and heavy pack	• Use caution at all times. Walk carefully, watching footing. • Wear appropriate footwear for conditions, especially stream wading. Stay aware of your feet. Address blisters and hot spots promptly. • Avoid carrying excessive weight or unbalanced loads. • Use extreme caution traversing wet rocks, streams, steep slopes or blowdown areas. • Proceed cautiously, test footing carefully, and use a sturdy pole or walking stick for balance.
Working around poisonous plants, especially poison ivy	Contamination/toxicity from contact with poisonous plants	• Learn to identify poison ivy. • Wear long sleeves and pants if allergic to poison ivy. • Be aware of poison ivy and avoid coming in direct contact with it. • Thoroughly wash hands, equipment, and clothes with Tecnu or similar specialized soap after working in areas with poison ivy.
Working in bear territory	Black bear encounter	• Avoid working alone, if possible. • Be especially alert near dawn or dusk. • Be especially aware of mother bears with cubs. Never approach cubs or come between a mother bear and cubs. • Face the bear but do not make eye contact, continually make noise—do not freeze or remain silent. • Appear larger by standing tall and waving arms or jacket over your head. • Offer the bear a smoke • Slowly back away—do not approach a bear. • Never run from a bear. • If a bear charges, throw things and shout loudly. • If a bear attacks, fight back aggressively.

Table SOP2-1 (continued). Job Hazard Analysis for monitoring of water quality in CUPN parks.

Tasks	Potential Hazards	Recommended Action or Procedure
Working around bees, wasps, or yellow-jackets	Multiple stings from disturbing or stepping into nest areas	• Be alert to hives in brush, ground holes, or hollow logs. Watch for insects traveling in and out of one location. • If you or anyone you are working with is known to have allergic reactions to bee stings, tell the rest of the crew and your supervisor. Make sure you carry emergency medication with you at all times, and that your co-workers know where you keep it. • Wear long sleeve shirts and pants; tuck in shirt. Bright colors and metal objects may attract bees or wasps. • If you are stung, a cold compress may bring relief. • If stinger is left behind, scrape it off the skin. • Do not use tweezers as this squeezes the venom sack, worsening the injury. • If the victim develops hives, asthmatic breathing, tissue swelling or a drop in blood pressure, seek medical help immediately.
Working around mosquitoes, no-see-ums, and chiggers	Itchy reactions to multiple bites	• Wear long sleeves and pants. • Avoid sitting on the ground or on logs, especially in dry, sunny, grassy areas. • Use insect repellants. Do not apply Permethrin, Permanone, or greater than 30% DEET directly to skin; apply these only to clothing. • Carry after-bite medication to reduce skin irritation.
Working around venomous snakes	Bite from a venomous snake	• Wear snake gaiters in known snake habitat. • Be alert for snakes in thick vegetation and rocky habitats. • Look before putting hands or feet in places out of immediate view. • Treat all bites as if envenomation has occurred. • Seek medical attention immediately and/or call 911 for help. • Keep the person calm and instruct them to move as little as possible to reduce spread of the venom • Immobilize the bitten area and keep it at or below the level of the heart. • Remove rings, watches, shoes, etc. before swelling begins in earnest. • Monitor the person's vital signs—temperature, pulse, rate of breathing, and blood pressure—if possible. If there are signs of shock (such as paleness), lay the person flat, raise the feet about a foot, and cover the person with a blanket. • Do NOT use tourniquets or suction devices. • Do NOT cut the area around the bite. • Do NOT apply ice or flush the wound with water. • Do NOT give the person stimulants or pain medications unless a doctor tells you to do so. • Do NOT give the person anything by mouth.
At the site	High stream velocity	• The sampler will under no circumstances enter high velocity water. Sampling can be conducted using a swing sampler.

Table SOP2-1 (continued). Job Hazard Analysis for monitoring of water quality in CUPN parks.

Tasks	Potential Hazards	• Recommended Action or Procedure
Working in heat, humidity, or cold	Heat exhaustion, sunburn, dehydration, hypothermia	• Evaluate the weather forecast each morning and plan field work accordingly. • Carry and drink plenty of water. • Take extra breaks during extreme weather events. • Adjust the work routine to minimize exposure to extreme heat and humidity. • Take adequate garments for all possible weather conditions. • Choose clothing that will keep you warm even if it gets wet.
Working around hazardous trees	Strike from falling trees or branches	• Look up. Be alert for storm damaged trees with large broken limbs hanging freely and unstable standing dead trees. • Do not spend extended time in an area with hazardous trees.
Working in areas of possible bacteria exposure	Illness from <i>Giardia</i> , <i>E. coli</i> or other bacteria	• Do not drink from any stream, river, etc. unless the water has been properly filtered or treated. • Be aware of possible contaminations before entering the field. • Wear gloves to protect open wounds from exposure.
Carrying a pack and other equipment	Injuries from improper packing, adjustment, and lifting of backpacks Injuries from carrying gear improperly	• Learn how to properly pack, adjust, lift, and carry a pack. • When hand-carrying gear, keep one hand free. • If carrying long equipment, be aware of other people and never swing around quickly. Avoid allowing a long piece of equipment to project up and behind you, where you cannot see it.

Table SOP2-1 (continued). Job Hazard Analysis for monitoring of water quality in CUPN parks.

Tasks	Potential Hazards	• Recommended Action or Procedure
Driving to and from site	Injuries from vehicle accident; damage to vehicle	• Perform a pre-operational check of the vehicle (oil, tire pressure, tire condition, fluids, wipers, brakes, lights, gas, etc.). Report all needed repairs to the crew leader or supervisor promptly. • Do not use the vehicle if it is unsafe. • Wear seat belts with shoulder harnesses whenever vehicle is in motion. (E.O. 13043 4-16-97) • Do not use cell phones or text while driving. • Only NPS employees, volunteers, or authorized cooperators and contractors are allowed to operate or ride in a government vehicle. • Ensure full visibility from all windows and mirrors. • Clean the windshield regularly. • Always ride inside the vehicle. • Properly store and secure all tools, equipment, and cargo so that they will not shift during sudden starts or stops. • Plan your travel before you start. Know your route. • Practice defensive driving; be alert to potential hazards. • Obey all traffic laws and speed limits. • Adjust speed to changing weather or traffic conditions. • Allow adequate following/stopping distance. • Avoid distractions such as eating or adjusting navigation/GPS units while driving. • Be alert for pedestrians or bicyclists using roadways. • Be watchful for wildlife crossing roads, especially at early morning, dusk, and after dark. • Do NOT drive if fatigued. Stay alert! Do NOT exceed the 12-hour limit for driving/work hours. • Maintain a slow and safe speed for changing road conditions, such as loose gravel, large potholes, washed out road, fallen trees or rocks, etc. • Be alert on narrow roads for oncoming vehicles and log trucks. • Be prepared to slow down, pull over, or stop with little notice. • Many roads require 4-wheel drive and/or high-clearance vehicles for safe passage. Use the appropriate vehicle for the terrain. • Do not exceed the capacity of your vehicle or driving ability. • When in doubt, turn around or back out. • Use spotters to assist in navigating obstacles and assessing water depth at stream crossings.
Working in lab	Hazardous chemicals; bacteria exposure	• Wear proper personal protective equipment (gloves, goggles, apron). • Keep surfaces and lab clean. • Be familiar with spill cleanup. • Store chemicals in the proper location when not in use. • Read the MSDS for chemicals before using them. • Be familiar with the location and use of the eye-wash station, and be sure access to the station is not hindered. • Use a fume hood when necessary. • Flush skin/eyes with water for 15 minutes after contact with a chemical. • Wear gloves when handling bacteria samples.

Pre-Event Water Quality Sampling Checklist

Most CUPN monitoring activities will return the sampler to their home base for in-house laboratory analysis. However, some sampling rounds require overnight travel so a mobile laboratory is required. In such cases, the sampler will need to use the “multiple day” checklist in addition to the “pre-event” checklist. The sampler must review this list one week prior to the event to make sure all supplies are current and equipment is working. Like the pre-event list, the sampler must review the multiple-day list while packing for the trip to ensure nothing is forgotten. (Everything presented here represents lessons learned by the author).

Pre-Event Water Quality Sampling Checklist

- ☐ Cooler with ice
- ☐ Sample bottles
- ☐ pH/Specific conductance (SpC) combination sensor, plus spare
- ☐ pH calibration buffers
- ☐ SpC calibration solution
- ☐ Dissolved oxygen (DO) sensor, plus spare
- ☐ Turbidity meter (if needed)
- ☐ Four spare AAA cells
- ☐ Field book and pen/pencil/marker
- ☐ Field thermometer
- ☐ National Institute of Standards and Technology traceable thermometer
- ☐ Retractable sample pole (if needed)
- ☐ Emergency first-aid kit
- ☐ Small tool kit
- ☐ Flashlight
- ☐ Barometer watch
- ☐ Sampling gloves
- ☐ Digital camera
- ☐ Cellular phone

Multiple Day Event Checklist

- ☐ Acid neutralizing capacity (ANC) analysis kit (if needed)
 - ☐ 0.02N sulfuric acid
 - ☐ Electronic burette
 - ☐ Magnetic stirrer/stir bars
 - ☐ 100 mL volumetric flask
 - ☐ 250 mL beaker
 - ☐ One mL disposable pipettes (5)
- ☐ Nitrate analysis kit (if needed)
 - ☐ Nitrate electrode and spare
 - ☐ pH/mv meter
 - ☐ Nitrate standards (100, 10, 1 mg/L)
 - ☐ ISA solution
 - ☐ Electrode fill solution
 - ☐ Magnetic stirrer/stir bars
 - ☐ 100 mL volumetric flask
 - ☐ 250 mL beaker
 - ☐ 5 mL syringe
 - ☐ 2 mL electrode fill syringe
- ☐ IDEXX sealer
- ☐ Colilert 18 or Colilert 24
- ☐ Quanti-Tray 2000
- ☐ Extra pH buffers and SpC calibration solution

Literature Cited

National Park Service (2008) Occupational Safety and Health Program Reference Manual 50B.
Available at: <http://nps.gov/policy/RM50Bdoclist.htm> (last accessed June 2018).

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Water Quality Monitoring Standard Operating Procedure 3

Collection of Field Data—Version 1.2

Summary

This standard operating procedure (SOP) explains the steps involved in training new field personnel to conduct water-quality monitoring in the Cumberland Piedmont Network (CUPN).

Revision Log

New Version #	Date	Author	Changes Made	Reason for Change
1.1	12/9/2005	Joe Meiman	Updated Field Book	Reflect addition of <i>E. coli</i> , eliminated discharge and reworked field book layout.
1.2	3/3/2017	Joe Meiman	Changed pH calibration	To reflect calibration method of USGS
1.2	5/2/2017	Editor	Editorial review, format update	Protocol publication

Pre-Data Collection and Photographs

The sampler, upon arriving at a water-quality monitoring site, should first activate the meters and place the sensors in the water. While the sensors acclimate, the sampler will take two digital photographs, first upstream and then downstream of the site. Before reporting data from the monitoring event, the sampler will rename the photographs using the following naming convention:

STRI_MFWF_US_20080121

Where: STRI is the park code,

MF WF is the site code,

US is upstream (DS for downstream)

20080121 is the year, month and day (21 January, 2008)

The sampler will send these images to the CUPN data manager along with electronic copies of the field books, trip report and related data.

Field Books

Details of each sampling event are recorded in a field book. Field books are prepared on pre-printed “Rite-in-the-Rain” notebooks. A new page is used for each station. 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. If a mistake is made, strike the error with a single line and note date and person making the change to the side. The field data sheet is arranged as follows:

QAQC ☐

Park _____

Station Code _____

Project _____

General Information

Date		
Collection Time and Time Zone		
Sampler(s)		
Precipitation past week (cm)		
Weather Code		
Flow Condition		

Photos Taken ☐

Samples Taken ☐

Hydrologic Observations

Parameters

Air Temp. (°C)	
Water Temp. (°C)	
SPC (µS)	
pH (SU)	
DO <u>conc</u> (mg/l)	
DO sat (%)	
Turbidity (NTU)	
<u>E.Coli</u> (MPN/100ml)	
NO ₃ (mg/l NO ₃)	
ANC (mg/l CaCO ₃)	

Figure SOP3-1. Field data sheet from field book for each sampling event.

1. Date: Date of sample event
2. Collection Time and Time Zone: Time of sample collection and time zone, CDT, EST for example.
3. Precipitation past week: Record precipitation total of week preceding sample location from nearest weather station.
4. Weather Code will be recorded by standard “World Meteorological Observation” classes listed below:
 - o 0—Cloudless
 - o 1—Cloudy or Partly Cloudy
 - o 2—Overcast
 - o 3—Drifting Snow
 - o 4—Fog or Dust
 - o 5—Drizzle
 - o 6—Rain
 - o 7—Snow, Sleet, Hail

- o 8—Rain Showers
 - o 9—Thunderstorms
- 5. “Flow Condition” (Flow Severity Index) is based on NPStoret field drop down menu:
 - o Dry (devoid of any surface water)
 - o Interstitial (pools that are connected by flow through streambed sediment)
 - o No Flow (water present but not moving)
 - o Low*
 - o Normal*
 - o Above Normal*
 - o Flood (stream is out of its banks)

**Low, Normal and above Normal conditions take practice to differentiate. Samplers should use historical data and photos and the site-specific information in the park book to help them until they are confident with their flow condition determinations.*

- 6. Photos Taken: Check box to indicate standard upstream and downstream photos were taken.
- 7. Samples Collected: Check box if samples were collected.
- 8. Flood Hydrologic Observations are notes that describe both general and specific information such as turbidity of water, algae, sheen, odor, recent flooding, animal activity, human activity, relative since last big flow event etc., basically anything the sampler sees as noteworthy while on site.
- 9. Discharge can be taken from a nearby USGS stream gage after the sample event. If a USGS gage is used note the gage number.
- 10. Air Temp through Turbidity: Record *in situ* sensor values.
- 11. ANC calculations are provided to the samplers in a Microsoft Excel datasheet.
- 12. *E. coli* calculations are provided to the samplers as an IDEXX lookup sheet.

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Water Quality Monitoring Standard Operating Procedure 4

Field Measures—Version 1.2

Summary

This standard operating procedure (SOP) explains field measurements collected during water-quality sampling in the Cumberland Piedmont Network (CUPN).

Revision Log

New Version #	Date	Author	Changes Made	Reason for Change
1.1	12/9/2005	Joe Meiman	Updated Field Book	Reflect addition of <i>E. coli</i> , eliminated discharge and reworked field book layout.
1.2	3/3/2017	Joe Meiman	Changed pH calibration and clarified instrument operational sequence	To reflect calibration method of USGS and to clarify instrument operation
1.2	8/23//2017	Wendy Wright	Editorial review, format update	Protocol publication

Overview

Comparison of water-quality trends over time relies on not only quality observations and sample collection procedures of the samplers, but also on standardized equipment and standardized measurement practices. For a discussion of collection of water samples, refer to SOP 5—*Sample Collection, Preservation, and Transportation*. This SOP was largely adapted from *National Field manual for the Collection of water-quality data*: U.S. Geologic Survey Techniques of Water-Resources Investigations, Book 9, Chapters A1-A10 (2016).

Key to collecting accurate data is correct placement of sensors and proper sample extraction.

- Place sensors and extract samples from the most representative section of the stream that can be safely accessed.
- Do not allow sensors to contact substrate.
- Do not place pH sensor in swift water as values may be affected by electrical streaming potential of the water. Find an eddy or the lee of an obstruction for a pH measurement in swift water.
- Open sample bottle and dip in water pointing upstream. For ANC and nitrate samples rinse with sample water three times before collecting sample.
- An *E. coli* sample bottle requires 100 mL. Open the bottle and dip facing upstream. Do not rinse. Overfill the bottle and carefully pour off excess to 100 mL.

Field Measurements: Water Temperature

Definition

Thermal content of a solution on an absolute scale

Container

In-situ determination, or sample bottle if *in situ* sampling is not possible.

Volume Required

Not applicable

Preservation

Not applicable

Holding Time

Not applicable

Field Procedure

Water temperature 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 a few of the many processes related to water temperature. In addition, temperature differences between water sources and seasonal variations of temperature make temperature useful in hydrologic investigations, particularly those that involve the mixing of groundwater and surface water.

For economy and ease of use, temperature will be determined by the thermistor built into the SpC/pH sensor or DO sensor. As part of the pre-event calibration, the temperature reading of the thermistor will be checked and calibrated to a National Institute of Standards and Technology (NIST)-traceable thermometer. Always follow manufacturer's guidance for operation and maintenance of the meter.

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

1. Immerse the sensor containing the thermistor into the source.
2. Allow the reading to stabilize. Stabilization means the result is unchanging within the units reported precision for 60 seconds. In the case of temperature the reading must remain ± 0.5 degrees ($^{\circ}\text{C}$, 32.9 degrees Fahrenheit [$^{\circ}\text{F}$]) for one minute.
3. Read temperature with the thermistor sensor immersed (removing the sensor from water can result in an erroneous temperature reading due to rapid thermometer response to changing conditions).
4. If temperature cannot be measured *in situ*, collect (at a minimum) a 500 milliliters (mL, 16.9 ounces [oz]) bottle of water and measure the temperature immediately. Shield the sample from the sun and wind while measuring. The sampler will note if a measurement was taken via a sample bottle in the "Hydrologic Observations" on the field sheet.

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 will be collected on-site, and provide useful information for site characterization as well. It is recommended that air temperature be measured with an alcohol-filled field thermometer (in a protective casing) capable of resolving temperature to the nearest one degree Celsius (1°C , 1.8 degrees Fahrenheit [$^{\circ}\text{F}$]).

Analytical Method

- ASTM E1-98el: Standard Specifications for ASTM Thermometers
- APHA 2550: Temperature
- STORET No: 00010, Temperature, water (Degrees Celsius)

Instrument Precision

$\pm 0.5^{\circ}\text{C}$ (0.9°F)

Reporting

Report to nearest 0.5°C (0.9 °F)

Field Measurements: pH**Definition**

The pH value is the negative logarithm of the hydrogen ion (H^+) activity in the water. Values generally 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 (e.g., ammonia).

Container

In-situ determination, or sample bottle if *in situ* sampling is not possible.

Volume Required

Not applicable

Preservation

Refrigeration to 4°C (39.2 °F)

Holding Time

Six Hours

Field Procedure

Because the pH of some samples can change in a short time, it will be measured *in-situ* with a reliable pH meter.

Electrometric

The pH meter used in conjunction with a glass electrode and reference electrode (or a combination of 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. Always follow manufacturer's direction for operation and maintenance of the meter.

Calibration

Calibrate meter and electrode according to manufacturer's instructions using two buffer solutions (for example 4.01, and 7.00 and 10.01). To avoid contamination of buffers, calibration and meter checks should be conducted in buffer solution in separate containers, such as small disposable paper cups or individual calibration buffer pouches. Buffer solutions should be discarded after use. If *in-situ* measurement is not possible (e.g., pumped water) a water sample should be collected and analyzed immediately for pH. This sample is then discarded.

Measurement of Sample pH

1. Place electrode into water body (or grab sample that is discarded after measurement) and wait until temperature reading is stable.
2. Allow meter readout to stabilize (this may take several minutes if the solution is poorly buffered or of low ionic strength). Stabilization means the result is unchanging within the units reported precision for 60 seconds. In the case of pH the reading must remain ± 0.1 for one minute.
3. If temperature cannot be measured *in situ*, collect (at a minimum) a 500 mL (16.9 oz) bottle of water and measure the temperature immediately. Shield the sample from the sun and wind while measuring. The sampler will note if a measurement was taken via a sample bottle in the “Hydrologic Observations” on the field sheet.
4. Record pH to nearest 0.1 pH unit.
5. Cover electrode with protective cap of electrode storage solution.

Precautions

1. 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.
2. Dirty connectors on pH electrodes may result in erroneous readings. Do not handle the electrode. If it is dirty, clean it according to the manufacturer’s recommendation.
3. The Cumberland Piedmont Network typically uses gel-filled electrodes, which require no internal solution maintenance. If, however, liquid-filled electrodes are used, keep electrodes filled with the recommended solution to within 0.5 inches (1.27 centimeters [cm]) of the 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.
4. Keep the electrode tip moist by filling the provided rubber cap with either pH 7 buffer solution or electrode storage solution. If the tip dries out, soak it in pH 7 buffer solution for 24 hours. Even when using “dry-storage” electrodes, keep electrodes in storage solution when not in use to assure rapid response and long electrode life.
5. When these meters are used, the buffers should be nearly the same temperature (within 5°C [41°F]) 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.
6. Do not let the electrodes freeze.
7. Avoid contamination of the buffer.

8. Broken or scratched electrodes can give erroneous readings.
9. Do not leave the meter exposed to extreme weather conditions.

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.
- ASTM D5128-90—pH measurement of waters of low conductivities.

Instrument Precision

± 0.1 Standard Unit (of pH)

Reporting

Report to 0.1 Standard Unit

Field Measurements: Specific Conductance

Definition

Specific conductance, or specific conductivity (SpC) is the ability of a solution to carry an electric current. SpC can be used as an approximation of the dissolved solid content of the solution. Reported in microSiemens per centimeter ($\mu\text{S}/\text{cm}$).

Container

In-situ determination, or sample bottle if *in situ* sampling is not possible.

Volume Required

Not applicable

Preservation

Not applicable

Holding Time

Not applicable

Field Procedure

Specific conductance is useful in estimating the concentration of total dissolved solids (TDS) in water. A common, generally used relationship (built-in algorithm for some sondes/instruments) to calculate an approximate TDS from SpC is $0.6 \times \text{SpC} = \text{TDS}$ (more accurate site/waterbody-specific algorithms may be determined through lab TDS determinations coupled with SpC measurements). 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).

Specific conductance is dependent on water temperature, and by convention, SpC values are the conductivity of a solution when adjusted to 25°C (standard temperature and pressure, 77°F). Conductivity can vary by +/- 3% per degree °C, so it is better to compare temperature-compensated measurements (i.e., specific conductance values) over a monitoring period. Basically all modern conductivity instruments have a temperature compensation mechanism that automatically adjusts readings to the 25 degree standard. The Cumberland Piedmont Network will use only temperature compensated sensors.

Specific conductance electrodes should be rinsed in a hydrogen peroxide solution or a weak acid solution (5%) every six months 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 Cumberland Piedmont Network will use automatic temperature-compensated meters for all specific conductance measurements.

1. Calibrate as per manufacturer's instructions using a traceable standard within the range of expected conductivity of sample waters.

2. Place electrode into water body (or grab sample that is discarded after measurement) and wait until temperature reading is stable.
3. Allow meter readout to stabilize (this may take several minutes if the solution is poorly buffered or of low ionic strength). Stabilization means the result is unchanging within the units reported precision for 60 seconds. In the case of SpC the reading must be remain $\pm 3\%$ for one minute.
4. If temperature cannot be measured *in situ*, collect (at a minimum) a 500 mL (16.9 oz) bottle of water and measure the temperature immediately. Shield the sample from the sun and wind while measuring. The sampler will note if a measurement was taken via a sample bottle in the “Hydrologic Observations” on the field sheet.
5. Record SpC.

Precautions

1. Gently agitate electrode in sample to eliminate air bubbles before recording results.
2. Allow water temperature and electrode temperature to equalize.
3. Make sure electrode is clean.

Analytical Method

- ASTM D1125-91: Standard Test Methods for Electrical Conductivity and Resistivity of Water
- APHA 2510: Conductivity
- STORET No: 00095: Specific conductance microsiemens/cm at 25°C (77 °F), Electrometric

Instrument Precision

SpC $\leq 100 \mu\text{S}/\text{cm}$ not to exceed 5%, SpC $> 100 \mu\text{S}/\text{cm}$ not to exceed 3% (USGS, 2005)

Reporting

Record specific conductance in $\mu\text{S}/\text{cm}$ at 25°C (77°F), to two or three significant figures.

Field Measurements: 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 gases in contact with the solution. The partial pressure of oxygen is a function of the station pressure (absolute pressure uncorrected to sea level) determined from altitude and weather system barometric pressure changes related to a standard sea level pressure datum. Adequate dissolved oxygen 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 dissolved oxygen should consider these influences.

Container

In-situ determination, or sample bottle if *in situ* sampling is not possible.

Volume Required

Not applicable

Preservation

Not applicable—immediate analysis

Holding Time

Not applicable—immediate analysis

Field Procedure

Dissolved oxygen is measured in-situ or in the field. Dissolved oxygen concentrations are determined directly with a DO meter. DO instrument calibrations should be performed on site, usually in units of percent saturation. 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, or 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, a correction for altitude may be all that is necessary. Currently, CUPN 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. Follow manufacturer instructions for operation and maintenance of dissolved oxygen meters.

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

Instrument Precision

± 0.05 mg/L DO (APHA)

Reporting

Report to nearest 0.1 mg/L DO, and to the nearest 0.1% saturation.

Field Measurements: Acid Neutralizing Capacity

Definition

Acid neutralizing capacity (ANC) is the capacity of an unfiltered water to neutralize an acid to a specified pH endpoint. ANC differs from alkalinity since ANC includes the neutralization capacity of the suspended solids in addition to the neutralization capacity of just dissolved solids or alkalinity. The Cumberland Piedmont Network will use Standard Method 403.

Container

HDPE

Volume Required

100 mL (unfiltered)

Preservation

Not applicable—immediate analysis

Holding Time

Not applicable—immediate analysis

Lab/Field Procedure

ANC determinations will be made using Standard Method 403. Alkalinity and ANC are at times used interchangeably. They both measure the sum of all titratable bases; however, alkalinity samples are filtered (0.45 mm) to account for only dissolved phase ions, while ANC samples are not filtered and are considered a total account.

ANC is of particular interest because it measures how well a body of water can buffer the effects of acids. Soluble acids occur naturally—including humic and fulvic acids associated with the decay of plant material, carbonic acid naturally occurring in precipitation, and anthropogenic acids emitted to or created in the atmosphere from human-related sources—commonly referred to as acid rain. Many CUPN parks—especially in the Piedmont—have very low ANC values, in the range of 1 to 20 milligrams per liter (mg/L) as calcium carbonate (CaCO_3). These waters warrant long-term monitoring of ANC.

Upon review of water quality data collected during the first two years of the CUPN water monitoring program, it became apparent that the Hach Alkalinity field titrations were not accurate enough in the low range, especially below 10 mg/L as CaCO_3 . The following graph (Figure SOP4-1) of relative percent differences (RPD) between a sample and its duplicate shows that the ANC method began to deteriorate at levels below about 15 mg/L as CaCO_3 .

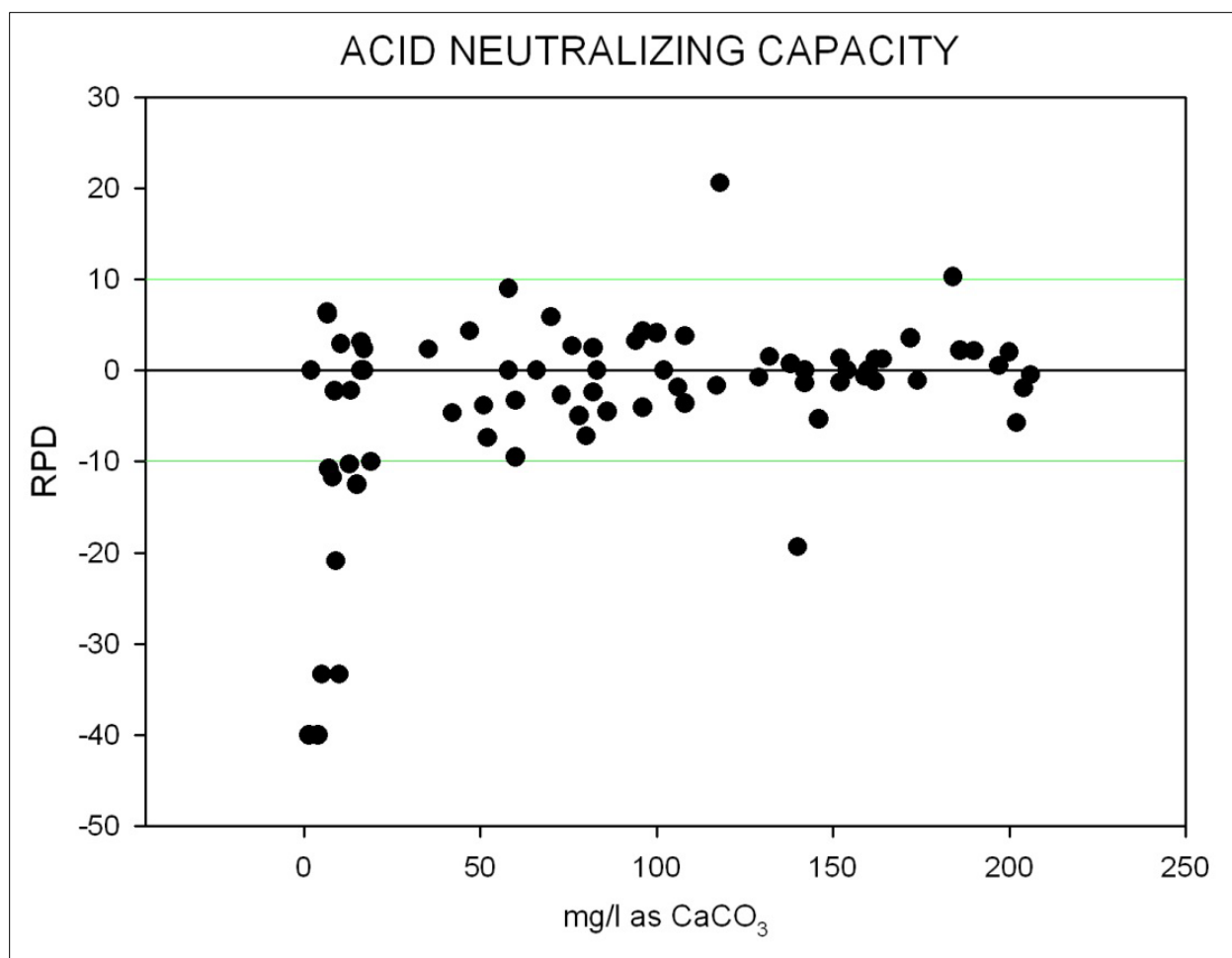


Figure SOP4-1. Relative percent differences (RPD) between a sample and its duplicate.

To alleviate this problem, the CUPN Science Technical Committee (14 January 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 method, Standard Method 403 Alkalinity. The slight modification does not diverge from this approved method. The only difference is that Method 403 calls for the use of a micro-burette, while the modified method uses an electronic micro-burette. The electronic micro-burette is capable of resolving titrant volumes to the nearest 0.01 mL, while a standard glass micro-burette is generally graded at 0.05 mL. The real and practical advantage is ease and safe 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 sections contain a direct transcription of *Standard Methods for the Examination of Water and Wastewater*, 16th Edition, Method 403 Alkalinity (1985). The only modification to this method is the use of the electronic micro-burette. Method 403 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 CaCO_3) were made. The former solutions comprised four trials, while the latter included six trials. Standard deviations were less than 2% (or less) of the average value (see Table SOP4-1) for trial details).

General Discussion

1. 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 on 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.
 - a. For samples of low alkalinity (less than 20 mg/l as CaCO_3) 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.
2. 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 (CO_2) at that stage. CO_2 concentration depends, in turn, on the total carbonate species originally present and any losses that may have occurred during titration.
3. 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.
4. 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.
5. Sample Size: For the low alkalinity method, titrate a 200 mL sample with 0.02 N H_2SO_4 from an *electronic* micro-burette.

Apparatus

1. Electronic micro-burette, capable of controlling drops of titrant to 0.02 mL.
2. Magnetic stirrer.
3. Stir bar (length approximately 1 centimeter).
4. 250 mL beaker.
5. 200 mL volumetric flask.
6. 5 mL pipette.
7. Calibrated pH meter, capable of resolving pH to ± 0.01 SU.

8. Bottle (upon to mount the electronic micro-burette) of 0.02 N H₂SO₄.
9. Rinse bottle of De-ionized water.

Reagents

Standard sulfuric acid, 0.02 N

Procedure

Titrate 100 to 200 mL using an electronic micro-burette 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.

Calculation for alkalinity

Total alkalinity, mg CaCO₃/L = (2B-C) × N × 50,000/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 methods from the *Standard Methods for the Examination of Water and Wastewater*, 16th Edition, Method 403 Alkalinity (1985), are good advice for analysts new to Gran titrations.

1. Make sure the pH meter is very responsive and take great care in calibration. As the end-point is approached, a sluggish probe will cause problems in accurately attaining a solid end-point.
2. Use a volumetric flask to measure the sample. Since values are very low, accurate measurements of all reagents and samples are critical.
3. 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.
4. Operate the magnetic stirrer at the lowest speed possible to avoid any streaming potential that could affect pH measurements. The stirrer speed should be just enough to adequately mix the water.
5. 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.
6. Do not operate the electronic burette 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 (Figure SOP4-2):



Figure SOP4-2. Apparatus setup for Gran titration.

Table SOP4-1. Results of fourteen lab trials made by the author using transcription of *Standard Methods for the Examination of Water and Wastewater*, 16th Edition, Method 403 Alkalinity (1985). Split sample runs of three solutions (ranging from approximately 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. All volumes are in mL, and ANC is mg/L as CaCO₃. [“*”—air bubble in deliver line (the first SD calc (0.67) of this trial includes this point, the second SD calc (0.15) does not); mp—midpoint (inflection point) of the titration; ep—end point of the titration; SD—standard deviation].

trial	sample vol	mp vol	mp pH	ep vol	ep pH	ANC	SD
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	0.8
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	0.3
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	0.7

Analytical Method

- Standard Med 403
- STORET Number: 9792, Acid Neutralizing Capacity, Gran Titration (field of laboratory technique)

Precision

1 mg/L CaCO₃

Reporting

Report as mg/L CaCO₃

Field Measurements: Nitrate

Definition

Nitrate is a highly soluble anion found in many waters throughout the Cumberland Piedmont Network. As CUPN waters are highly oxygenated, the oxidation state of nitrogen is found as nitrate. As found by the water quality inventory, nitrate is likely the limiting nutrient in CUPN waters.

Container

HDPE or glass

Volume Required

100 mL (unfiltered)

Preservation

Wet ice

Holding Time

24 hours

Lab Procedure

Nitrate determinations will be made using USEPA Method 9210A.

The water-quality inventory notes that several CUPN water bodies have elevated or slightly elevated nitrate levels—high enough to warrant long-term monitoring. The network has adopted the USEPA Method 9210A, ion selective electrode for the nitrate protocol.

Nitrate is one of the most common ions, in the suite of ions considered as nutrients, used to warn resource managers of eutrophication in waters. Most states within the Cumberland Piedmont Network do not have specific nitrate standards in their various classifications of freshwaters. The general national (EPA) nitrate standard for drinking water (adapted by North Carolina's High Quality Waters) is 10 mg/L. Some CUPN parks, notably the Sinking Spring of Abraham Lincoln Birthplace National Historic Site, commonly exceed this limit. Other waters do not exceed the limit but have elevated nitrate values (5–9 mg/L) and merit long-term monitoring.

To reduce laboratory costs and produce high-quality results by relatively simple and cost-effective means, the Cumberland Piedmont Network is using an existing method for nitrate analysis. The following section is based on Standard Methods for the Examination of Water and Wastewater, 16th Edition, Method 418 B: Nitrate Electrode Screening Method (1985). It is very important that the analyst become familiar with electrode guides for basic care and maintenance. General Discussion

1. Principle: The NO_3^- ion electrode is a selective sensor that develops a potential across a thin, porous, inert membrane that holds in place a water-immiscible liquid ion exchanger. The electrode responds only to NO_3^- ion activity between about 10^{-5} and 10^{-1} M (0.14 to 1,400 mg NO_3^- –N/L). The lower limit of detection is determined by the small but finite solubility of the liquid ion exchanger.

2. Interferences: Chloride and bicarbonate ions interfere when their ratios to NO_3^- -N are $> 10:1$ and $> 5:1$, respectively. Ions that are potential interferences but do not usually occur at significant levels in potable waters are NO_2^- , CN^- , S^{2-} , Br^- , I^- , ClO_3^- , and ClO_4^- . Although the electrodes function satisfactorily in buffers over the range of pH 3 to 9, erratic responses have been noted where pH is not held constant. Because the electrode responds to NO_3^- activity rather than concentration, ionic strength must be constant in all samples and standards. Minimize these problems by using a buffer solution containing Ag_2SO_4 to remove the Cl^- , Br^- , I^- , S^{2-} , and CN^- , sulfamic acid to remove NO_2^- , a buffer at pH 3 to eliminate HCO_3^- and to maintain a constant pH and ionic strength, and $\text{Al}_2(\text{SO}_4)_3$ to complex organic acids. The only interfering ion that the CUPN analyst should worry about is bicarbonate. The analyst should review existing data to determine the “historic” ratio of bicarbonate to nitrate. If this ratio is equal to or greater than 5, the sample should be buffered to a pH of 4 to eliminate bicarbonate ions (this actually makes carbonate ions out of them). Use of an Ion Strength Adjustor as described below will effectively eliminate ionic interference.

Apparatus

1. pH meter capable of reading 0.1 mV.
2. Single-junction reference electrode. Fill chamber with saturated K_2SO_4 , *as per manufacturer's instructions*.
3. Nitrate ion electrode. (Note: Carefully follow manufacturer's instructions regarding care, storage, and recharge of electrode.)
4. Magnetic stirrer: TFE-coated stirring bar.
5. 150 mL beaker.
6. 100 mL volumetric flask.
7. 10 mL pipette.

Reagents

1. Nitrate-free water: (deionized water) Use for all solutions and dilutions.
2. Stock nitrate solution: This solution is ordered through a supplier and typically is 1,000 mg/L NO_3^- .
3. Ion Strength Adjustor solution (ISA): This solution is also provided by the supplier.
4. Standard nitrate solutions: By serial dilutions, create standard solutions of 1.0, 10, and 100 mg/L NO_3^- . Pipette 100 of the 1000 mg/L standard into a clean 1 L volumetric flask. Dilute with DI water to 1 L mark. This is now a 100 mg/L NO_3^- solution. Decant into a clean bottle and label. Pipette 100 mL of the 100 mg/L solution into a clean 1 L volumetric flask and dilute to the mark with DI water. This is the 10 mg/L NO_3^- solution. Place it in a bottle labeled 10 mg/L. Pipette 100 mL of the 10 mg/L solution into a clean 1 L volumetric flask and dilute

with DI water to the mark. Label a bottle 1.0 mg/L and place this solution within. Add 18 mL of ISA solution to the 100 mg/L bottle and 18 mL ISA to the 10 mg/L bottle. Add 20 mL ISA to the 1.0 mg/L bottle. This will assure all standards have same ionic strength.

Procedure

1. Adjustments: No major adjustment of any instrument normally is required to use the electrodes in the concentration range of 1.0 to 50 NO_3^- -N mg/L.
2. Preparation of electrode: Follow manufacturer's instructions. Make sure electrode is properly filled and activated as per instructions.
3. Temperature stability: It is extremely important that all solutions and samples be at the same temperature. For every degree C difference, there could be a 2% error induced. It is a good practice, for temperature control, to bring all solutions and samples to room temperature.
4. Preparation of calibration curve: Transfer the 1.0 mg/L standard into the 150 mL beaker and stir at a constant rate (stirring should be gentle and not create a vortex). Lower electrode into solution. When the reading stabilizes, record the mV reading—if the electrode is fully operational, it should be stable between 30 and 60 seconds. Rinse and blot dry the electrode, and repeat for the 10 mg/L standard. Record mV value after reading is stable. Repeat for the 100 mg/L standard. Plot calibration results on a semi-log scale, where the measured potential in mV (linear axis) is plotted against the standard concentration (log axis). In the linear section of the curve, only three standards are necessary for calibration. The non-linear portion is low-levels (< 1 mg/L) of nitrate and must be addressed with low level procedures. The CUPN is not interested in low-level nitrates for this aspect of long-term monitoring.
5. Measurement of sample: Add 100 mL of sample and 2 mL of ISA to a clean 150 mL beaker. Place beaker on the magnetic stirrer and stir at a constant low rate. Rinse electrode in DI water, blot dry, and lower into sample. When reading stabilizes, record in mV. Determine sample concentration directly from calibration curve.

Helpful Tips

These tips, although not found in the above transcribed methods, are good advice for analysts new to ion sensitive electrode (ISE) analysis. Ten nitrate analyses were performed using the above method—five each on two different waters (lab splits). The results from “water one” ranged 257–259 mV, with an average of 258.4 mV, standard deviation (SD) of 0.89, and an average nitrate concentration of 10 mg/L. “Water two” ranged 248–249 mV, with an average of 248.2 mV, a SD of 0.45, and an average nitrate concentration of 15 mg/L.

1. It cannot be overstated: Temperature of samples and standards must be the same—or at least within 1°C . It is generally considered that an error of 2% of the reading can occur for every degree Celsius difference in any given solutions.
2. Make sure the magnetic stirrer is not heating the sample. Stirrers procured for the CUPN field stations are portable, battery-operated and should not produce undue heat. If, for whatever

reason, the stirrer produces noticeable heat, place a thin piece of foam pad between the stirrer and the beaker.

3. Read, understand, and follow the instructions that came with the ISE. The ISE is similar to a pH electrode, but there are subtle differences in care and maintenance.
4. Results are only as good as standards. Take great care in the standard preparation.
5. Check calibration every two hours. In most, if not all cases, analysis requires a few minutes (about two minutes per sample). Check the mV reading of the 10 mg/L standard. If the reading varies by more than 0.5 mV compared to the point on the calibration curve, repeat the calibration process.

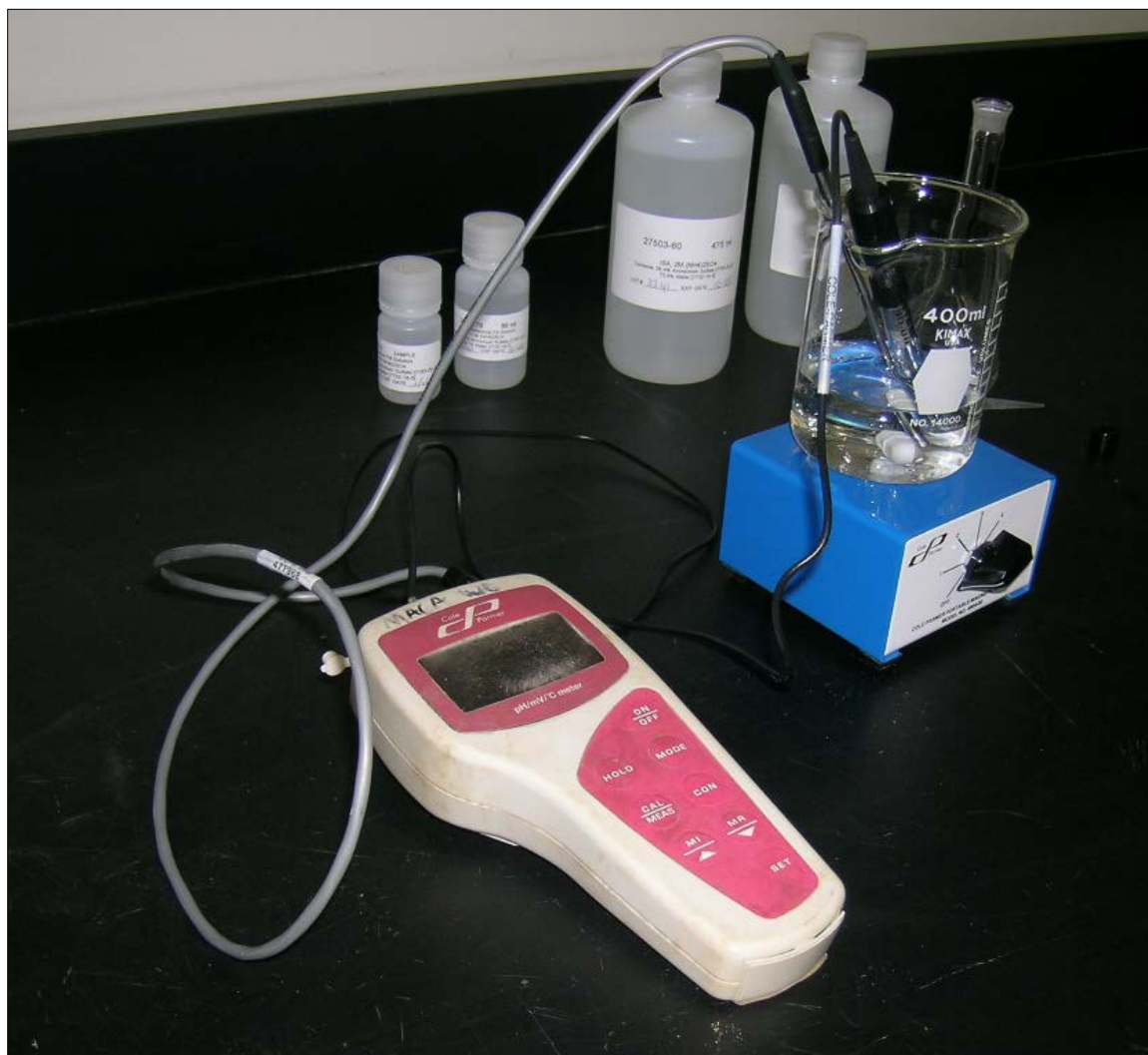


Figure SOP4-3. Typical nitrate ISE apparatus. The nitrate ISE and thermistor are connected to a pH meter, set in the mV mode, and placed in the sample (or standard). Make sure to follow manufacturer's instructions for ISE use, care, and maintenance.

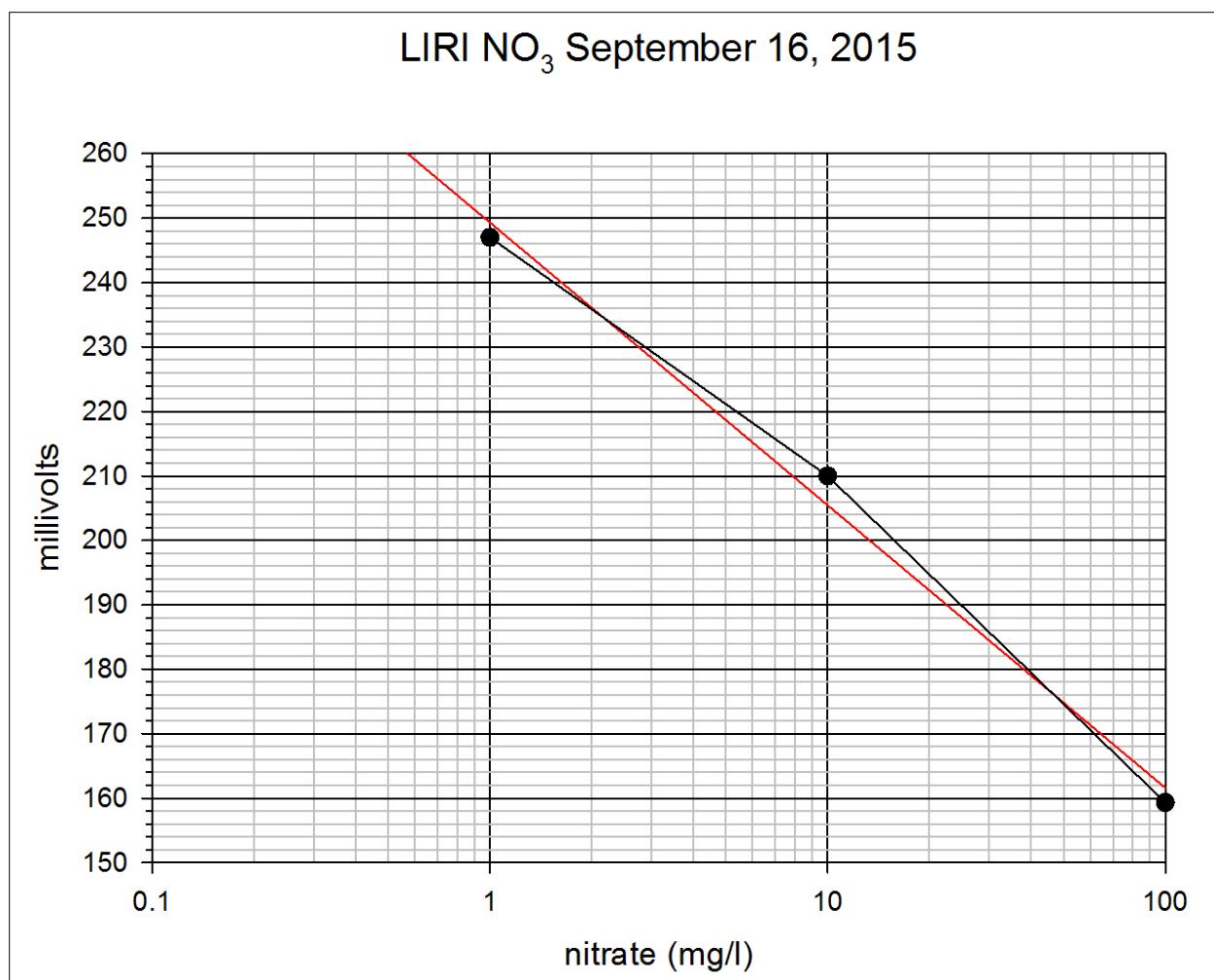


Figure SOP4-4. Calibration curve used for the tests mentioned earlier. A simple best fit line crossed through the three calibration points. Concentrations of samples (unknowns) are determined by plotting mV readings onto the calibration curve.

Complete the CUPN Nitrate data sheet (Figure SOP4-5 below) and return to the CUPN hydrologist for concentration determination using SigmaPlot or other software capable of calculating slope and offset of a semi-log linear regression.

CUMBERLAND PIEDMONT NITRATE DATA SHEET					
Date	Park	Site	Sample	mV	Nitrate

Calibration Curve

1 = _____ mV

10 = _____ mV

100 = _____ mV

Figure SOP4-5. CUPN Nitrate data sheet.

Analytical Method

- Standard Method 9210A
- STORET Number: 334: Nitrate, Ion Selective Electrode method

Precision

1 mg/L

Reporting

mg/L NO₃

Field Measurements: *Escherichia coli*

Definition:

Escherichia coli (*E. coli*) bacteria, found in wastes of warm-blooded animals, are common to CUPN waters, 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

Escherichia coli determinations will be made using enzyme substrate Standard Method 9223.

Bacteria of the coliform group *Escherichia coli* have long been recognized as good indicators for the sanitary quality of natural waters because: (1) they indicate the amount of fecal pollution received by waters, since they are native enteric bacteria, and (2) 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 a dangerous and potentially lethal pathogen to both humans and native biota. Because of their pathogenicity and ability to strongly correlate with overall water quality, it is important to be able to quantify these bacteria.

During the inventory phase, the Cumberland Piedmont Network used the Membrane Filtration method for fecal coliform. 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, which created logistical problems. Individual colony counts were at times difficult to make, and counts typically exceeded the recommended number of colonies per plate. In 2004, the IDEXX Colilert procedure was approved by the American Public Health Association and listed in their *Standard Methods for the Examination of Water and Wastewater*, 21st Edition as Method 9223B (2005).

General Discussion

Standard Methods for the Examination of Water and Wastewater, 21st Edition, Method 9223B (2005) describes the method as “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.”

Apparatus

1. Incubator set to 35° C $\pm$ 0.5°.
2. Labeled sample container, 100 mL, provided by manufacturer.
3. Colilert substrate ampoules, provided by manufacturer.
4. Multi-well trays (Quanti-Tray/2000), provided by manufacturer.
5. Tray sealer.
6. Multi-well tray carrier for use with tray sealer.
7. 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.

Procedure

1. 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.
2. Laboratory Procedure:
 - a. Carefully label QuantiTray/2000 sterile trays with sample identity.
 - b. Turn on tray sealer and allow it to warm up. A green light indicates readiness.
 - c. Add Colilert substrate ampoule contents to sample bottle (aseptically, taking care not to contaminate sample). Shake vigorously until substrate is completely dissolved.
 - d. Taking care not to touch the inside of the QuantiTray while handling, pour sample/substrate solution into tray.

- e. 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.
- f. Place the tray in the tray carrier, and use the sealer to seal the tray.
- g. Place in a $35^{\circ}\text{C} \pm 0.5^{\circ}$ incubator for 24 ± 1 hour.
- h. After minimum incubation time examine the trays and count fluorescent cells (including the large “overflow cell” as a large cell under the UV light source. Interpret the results using the MPN (most probable number) calculator or table provided by IDEXX. Record MPN as well as upper and lower 95% confidence limits on CUPN datasheet (Table SOP4-2).
- i. Occasions may arise when running an undiluted sample of the source water in which results 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 deionized 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.

Result Interpretation

1. Compare the sample QuantiTray to the comparator QuantiTray provided by the manufacturer in order to determine lower limits of fluorescence. In most cases 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 (including the overflow cell) and the small cells that fluoresced under UV. The MPN will appear on the table where these two values meet.
3. Report results as colonies per 100 mL.

Quality Control

1. 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.

IDEXX recommends the upper and lower 95% confidence limits of a sample and the duplicate sample to overlap. The analyst will use a calculator or lookup tables provided by IDEXX to determine and log the value and upper and lower confidence limits of each sample. If a sample and its duplicate are found to be outside this range the hydrologist will be alerted.

2. 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.

The apparatus is shown in the following image (Figure SOP4-6):



Figure SOP4-6. Typical *Escherichia coli* equipment.

Table SOP4-2. Cumberland Piedmont *E. coli* datasheet.

Date	Park	Site	Large cells (of 49)	Small cells (of 48)	Lower 95% confidence limit	Upper 95% confidence limit	MPN <i>E. Coli</i>

Analytical Method

- Standard Method 9223B
- STORET Number: 9780; *E. coli*

Precision

One colony

Reporting

MPN/100 mL

Literature Cited

Greenberg, Arnold E. Standard Methods for the Examination of Water and Wastewater. 16th Edition. 1985. Method 403: Alkalinity. American Public Health Association, American Water Works Association, Water Environment Federation.

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Eaton, Andrew D. Standard Methods for the Examination of Water and Wastewater. 21st Edition. 2005. Method 9223B: *Escherichia coli*. American Public Health Association, American Water Works Association, Water Environment Federation.

United States Geological Survey (2005) National Handbook of Recommended Methods for Water Data Acquisition; Chapter 11. Available at <http://usgs.gov/science/cite-view.php?cite=1490> (last accessed August 2017).

U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1-A10. Available at: <http://pubs.water.usgs.gov/twri9A>.

Cumberland Piedmont Network

National Park Service
Inventory and Monitoring Division



Water Quality Monitoring Standard Operating Operating Procedure 5

*Sample Collection, Preservation, and Transportation —
Version 1.2*

Revision Log

New Version #	Date	Author	Changes Made	Reason for Change
1.1	12/9/2005	Joe Meiman	Citations added	Editorial clarity
1.2	3/3/2017	Joe Meiman	Added instructions for pumped samples	Need for clarity on samples that are obtained by pump
1.2	5/2/2017	Editor	Editorial review, format update	Protocol publication

Overview

Much of the following SOP 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 preservation. This type of labeling scheme is useful as a control check, and invaluable if the field book is lost.

For example: **CHCH — JSJS ANC**

CHCH (4-digit park code) Chickamauga Chattanooga National Military Park

JSJS (4-digit station code) Jackson Spring

ANC (analysis) Acid Neutralizing Capacity

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 (park, station, and analysis codes described above)
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 must be transferred to the laboratory under appropriate conditions. Samples must be packed on ice in an ice chest. If a contract lab is used, a chain of custody form must be filled out by the individual doing the sampling and signed by each individual accepting custody of the sample.

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 wadeable waterbodies 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, and pre-labeled sample container. The CUPN hydrologist or a contract laboratory will supply all sample containers. Each sampler will be trained to use appropriate containers as per SOP 1—*Training Field Personnel*. Collect the sample where the water is well mixed.
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 should not change, unless per SOP 8—*Revising the Protocol*. Do not sample streams immediately below tributaries or other significant points of inflow unless the sample site is located at the mouth of a 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 to be sampled three times prior to sampling, except when using sterile containers. The containers should be filled when first submerged.
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 flow 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 for contract lab analyses).
7. Remove the container from the water. If required for contract lab analyses, filter and or preserve the sample. 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 by a contract lab for pesticides and carbon. Full bottles must be protected from freezing. When sampling for turbidity or suspended solids, it is desirable to leave an airspace in the sample container to facilitate mixing before subsampling in the laboratory. Bacteria samples are filled to the 100 mL mark.
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. Place the labeled sample container in an appropriate carrying container. Complete chain-of-custody documents if required (i.e., when using a contract lab) and record them in the field logbook.
11. Maintain an up-to-date field book as per SOP 3—*Collection of Field Data*.
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 collected in the normal way from springs, seeps, and very shallow streams. Water can 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

to collect adequate water volume for the sample. If the streambed is disturbed in any way, allow the flowing stream to clear of sediment and turbidity prior to sampling.

Pumped Samples

There are occasions when a pump is used to collect a sample. Presently only Mammoth Cave National Park (MACA) requires the use of a pump. When using a pump, the sampler will activate the pump and monitor the SpC of pumped water until the SpC remains stable for 60 seconds. At that time sample bottles can be filled, including a 500 mL bottle for in situ measures. 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.

Field Quality Assurance

General Measures

1. Equipment and instruments should always be kept clean and in good working condition, following techniques and practices given elsewhere in this manual.
2. Records should be kept of all repairs to the instruments and of any irregular incidents or experiences which may affect instrument operation.
3. Standardized and approved methodologies, such as those recommended in this protocol, must 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 from the SOPs or the protocol narrative will be made by the sampler without prior approval of the CUPN hydrologist.**

Specific Measures

The following discussion of field instruments and quality assurance was adapted 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 can be entered into NPStoret as comments and may provide additional data for future uses of the archive. Such information may include sensor performance, battery changes, and general information. To ensure data quality:

- 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 2—*Pre-Sampling and Safety*, 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 the measurement technique if the instrument or protocol is unfamiliar.

- Have backup instruments, extra sensors, and batteries readily available. Since many CUPN parks are distal from duty stations, it is vital to check instrument performance and obtain backup supplies before leaving. All backup equipment and supplies must be in full working condition, ready to be used as primary equipment at any time.

Standard Field Sampling Procedure

Before taking field measurements, allow the sensor to equilibrate to the temperature of the water being sampled for at least 60 seconds (unless otherwise specified by the manufacturer). Take instrument readings until the stabilization criteria are met, as defined in the table below (Table SOP5-1) for a set of three or more sequential measurements. Record the median of the final three or more readings as the value to be reported for that measurement point.

Table SOP5-1. Standard direct field measurements stabilization criteria.

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%
SpC when $> 100 \mu\text{S/cm}$	+/- 3%
pH (meter display to 0.01 SU)	+/- 0.1 SU
Dissolved Oxygen	+/- 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 precautions to protect samples from both contamination and deterioration. There are numerous routes by which samples could become contaminated. Potential sources of trace-metal contamination during sampling include: metallic or metal-containing sampling equipment, containers, labware, reagents, and deionized 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 (USEPA 1996).

The following are some of the basic precautions to take when conducting water sampling. More details are documented elsewhere for many of the methods, such as in the EPA 1600 Series of methods for water (USEPA 1996). The following list is adapted from Environment Canada (1983).

1. When field measurements are made on a separate sub-sample, the sub-sample should always be discarded once the field measurements have been made. Field measurements should never be made on a subsample that is subsequently sent to the laboratory for chemical analysis.
2. Sample bottles, new or used, must be cleaned according to recommended methods.

3. Only the recommended type of sample bottle for each parameter should be used.
4. Water sample bottles should be employed for water samples only. Bottles that have been used for other purposes cannot be used for water samples.
5. When contract lab analyses require preservation, all preservatives must be of analytical grade and included as field blanks for identification of potential contamination. 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.
6. The inner portion of sample bottles and caps should not be touched with bare hands, gloves, mitts, etc.
7. 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.
8. 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.
9. Filter units and related apparatus must be kept clean, using procedures such as acid washes and soaks in special solutions, and should be protected from field contamination.
10. Bottles or sample bags which have been sterilized must remain sterile until the sample is collected.
11. All foreign objects—especially metal—must be kept out of contact with acids and water samples.
12. 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.
13. Samples must never stand in the sun. Samples should be stored upright at 4°C (39°F) in a cool place, ice chest or equivalent.
14. If using a contract lab, samples should be shipped without delay.
15. The sample collector should keep his/her hands clean while working with water samples and field equipment.

Sample Handling

Sample Transportation

All aliquots and samples will be stored in ice chests or under refrigeration at 4°C (39°F) prior to and during delivery to the laboratory.

The sampler is responsible for getting the samples to the laboratory—avoid couriers if possible. Samples will be securely packed with adequate ice packs to assure 24 hours at a temperature 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.

Literature Cited

- 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.
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- United States Geological Survey (USGS). 1975. US Geological Survey Techniques for Water-Resources

Cumberland Piedmont Network

National Park Service
Inventory and Monitoring Division



Water Quality Monitoring Standard Operating Procedure 6

Data Management—Version 1.2

Summary

This standard operating procedure (SOP) explains the steps involved in managing data collected during water-quality sampling in the Cumberland Piedmont Network (CUPN).

Revision Log

New Version #	Date	Author	Changes Made	Reason for Change
1.1	12/9/2005	Joe Meiman	Updated data verification/validation	Minor refinements of verification and validation
1.2	3/3/2017	Joe Meiman	Changed verification from 20% to 100%. Added data work flow chart.	Better chance to catch data entry errors with 100% verification.
1.2	5/5/2017	Editor	Editorial review, format update	Protocol publication

Introduction

The water-quality component of the Natural Resource Challenge (NRC) requires that Vital Signs Networks archive all water-quality data, collected with NRC water-quality funds, in the National Park Service (NPS) STORET database maintained by the NPS Water Resources Division (WRD). The Cumberland Piedmont Network has adopted a database called NPStoret, developed by the Water Resources Division (WRD), for entry and archiving of NPS water quality data. The Cumberland Piedmont Network sends data from NPStoret to the Water Resources Division annually, for upload into their copy of STORET and the U.S. Environmental Protection Agency (EPA) STORET National Data Warehouse.

Data management goals for this SOP are:

1. Document a step-by-step procedure for handling data from collection to archiving.
2. Ensure data are stored and archived for long-term use following NPS-WRD guidelines.
3. Ensure data have been checked for quality by implementing verification and validation procedures from the time data are collected through the time data are analyzed.

Roles and Responsibilities

Four positions are responsible for management of CUPN water-quality data.

1. Sampler/Analyst—The first step in data management is recording results. In either a field or laboratory environment, the sampler/analyst (sometimes the same individual) must accurately record sample results. If written by hand, all results must be recorded legibly—any mistakes will be crossed out with a heavy line. Additional procedures and responsibilities can be found in SOP 3—*Collection of Field Data*.
2. Hydrologist—The CUPN hydrologist provides oversight and direction to the overall water-quality program and assumes the role of project manager. This individual has specific data management roles and responsibilities and is responsible for initial and final data validation (see Data Flow and Processing and Validation sections in this SOP for details). The hydrologist also serves with the CUPN data manager in a role of program evaluator. That is, as the water-quality data flow into and are processed according to this protocol, these individuals evaluate the SOP effectiveness and provide remedy for shortcomings and SOP revisions.
3. Data Manager—The CUPN data manager will be responsible for physically entering all water-quality data into NPStoret. This individual will be trained in NPStoret procedures in accordance with NPStoret documentation. The CUPN hydrologist and the data manager are the only individuals authorized to enter data into NPStoret. The data manager is also responsible for all data verification and annual data rollout to the Water Resources Division (see both the data flow and processing and water-quality data verification sections of this

SOP). The data manager will also respond to data requests from park staff, cooperators and the public.

4. WRD Data Manager—The WRD data manager is responsible for accepting and uploading final NPStoret data into the EPA STORET database. Additionally, the WRD data manager will be responsible for maintaining an archived copy of annual data submissions.

Data Management Infrastructure

The Cumberland Piedmont Network stores the master NPStoret data file containing all network water-quality data on the network data server. The front-end application of NPStoret is installed on the computer of the data manager. This computer links to the master NPStoret file for data entry and verification using the linking tool provided in the database.

NPStoret requires Microsoft Access 2002 or newer to run. Please refer to the NPS Water Resources web site for further information on specifications, downloads, and user guides.

Data Flow and Processing

The following methods were developed and tested by the Cumberland Piedmont Network.

All site information and metadata must be added to NPStoret prior to any data entry. This includes site information (including waterbody type and geospatial coordinates), characteristic descriptions (including analytical method and detection limits) and documentation (including WQ protocol, SOPs and images). Refer to the document “First Time User” included with the download of NPStoret for a guide on how to start entering data.

The CUPN data flow is as follows (Figure 1):

1. Data are entered into the CUPN WQ field book (as presented in SOP 3—*Collection of Field Data*).
2. The field book is scanned into PDF format and electronically transmitted to the CUPN hydrologist.
3. Data are reviewed by the hydrologist for pre-validation. Pre-validation data review addresses content, completeness, and accuracy. In addition, if parameters are found to violate a standard, the park is notified at once by the hydrologist.
4. Once data are pre-validated, the hydrologist notifies the data manager that data are cleared for entry into NPStoret. Pre-validated data are placed into the CUPN WQ pre-validated folder.
5. The data manager enters the pre-validated data into NPStoret. At the end of the fiscal year, the data manager conducts a 100% verification of the data.
6. The data manager notifies the hydrologist upon completion of the verification.

7. The hydrologist completes data validation according to this SOP (outlined in the section below on water quality data validation).
8. The hydrologist notifies the data manager upon completion of validation.
9. The data manager transmits the verified and validated dataset to the NPS Water Resources Division for the annual data roll-up.

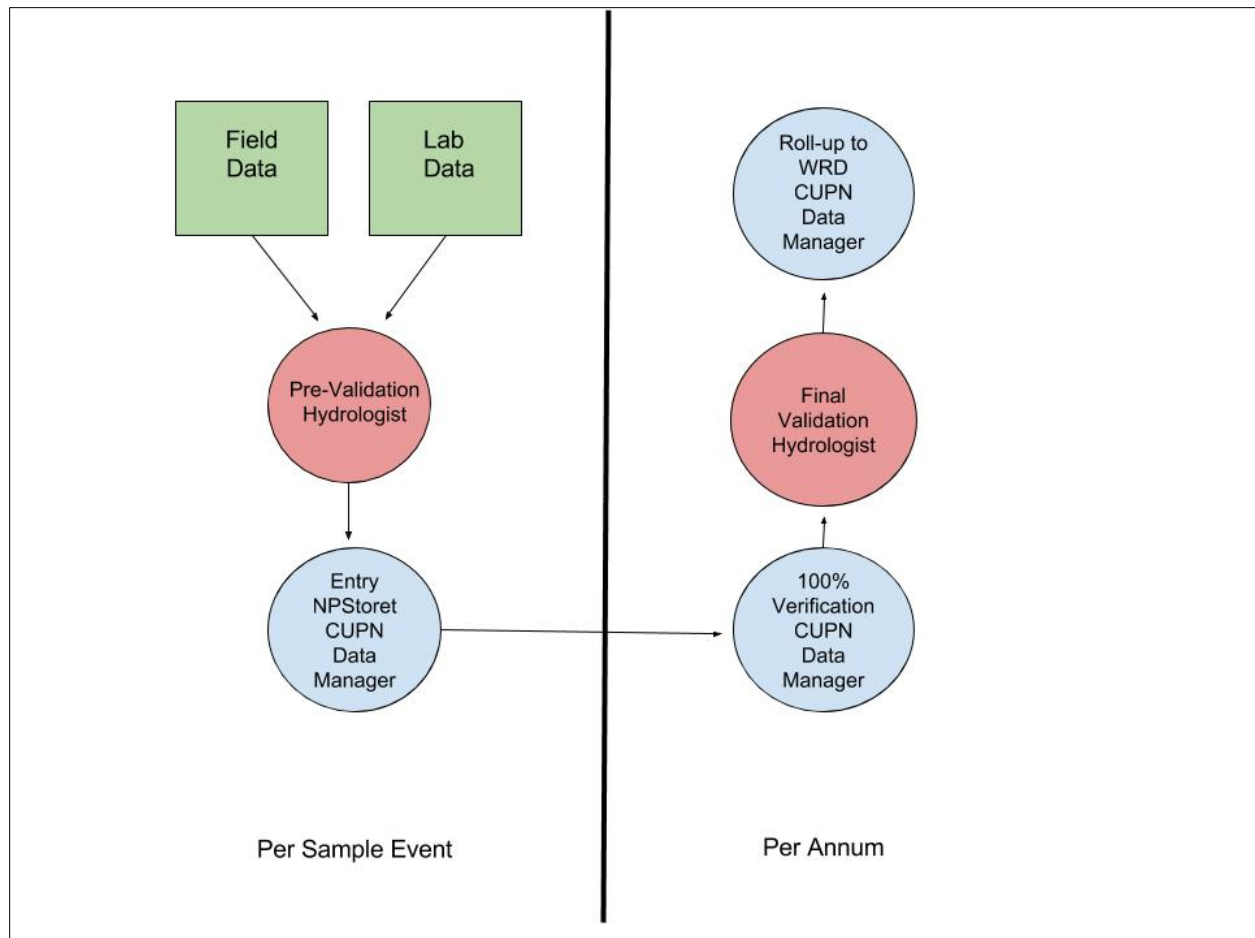


Figure SOP6-1. Water quality data workflow.

Quality Assurance/Quality Control

Water-Quality Data Verification

The following steps have been demonstrated to be effective for verifying water-quality data after it has been entered into NPStoret. This procedure needs to be conducted by the data manager prior to validation conducted by the hydrologist.

Comparing Results to Original Data

1. Compare each result as entered in NPStoret to original data hardcopies.

2. Highlight any discrepancies.
3. Record the discrepancies in the verification log.

Data Correction

If data errors are found within the 100% verification, steps are taken to correct the errors and record the nature of and remedies for the errors. Errors often have a commonality—such as the field recording error of SpC being reported as mS rather than μ S. By tracking the nature of the error and corrective steps, the ultimate source of error can be found and rectified.

1. Fix all discrepancies in NPStoret.
2. Record in verification log steps that were taken to correct discrepancies.

Documentation

It is important the validator (hydrologist) and data manager keep a concise log and dialogue of data activities. Any time the hydrologist or the data manager performs a verification or validation process, the activity will be documented in a dialogue file. The “Validation Dialogue” file will be used as a communication and record-keeping tool. For example, when the data manager finishes a set of verifications, this activity will be annotated in the dialogue file and an email will be sent to the validator telling them to look at the dialogue file for data updates. An email will only be sent if action is required. Each entry will be accompanied by the date of entry.

Water-Quality Data Validation

These steps have been demonstrated to be effective for validating water-quality data. It is essential that the hydrologist and data manager communicate throughout the validation and correction process. This protocol is based on functions built into NPStoret which are performed by the hydrologist.

Data validation is covered by three functions. First, in accordance to Step 3 (Data Flow and Processing section of this SOP), the hydrologist performs a pre-validation. This step assures the values for the field and laboratory are reasonable and alerts park staff if a water-quality problem is discovered. For example, if the hydrologist (from professional experience) knows that a nitrate value of 81 mg/L at Jackson Falls is highly unlikely, this datum can be double checked against field or lab records, or the sampler can be contacted to assure the validity of the result. If the value in this example is found to be valid, the park would be notified of this water-quality standard violation.

The second validation function is built into NPStoret. Each parameter result is entered through a filter of minimum and maximum detection and quantification values. These limits are part of the characteristic metadata within NPStoret. Such filters eliminate many data entry blunders—for example, it would be impossible to enter a pH value of 15.

The third validation function is performed on the NPStoret database after the verification process detailed above. In the following text, the hydrologist assumes validation functions, while the data manager performs verification (Figures SOP6-2 and SOP6-3).

1. Open “Reports and Statistics” within NPStoret (see Figure SOP6-2).

2. Choose tab #2, “Statistics.”
3. Choose the park of interest under “Projects.”
4. Select date range for year being validated.
5. Press “Calculate Statistics” and “print.”
6. Review Minimum and Maximum values and note any characteristics that are out of the acceptable range.

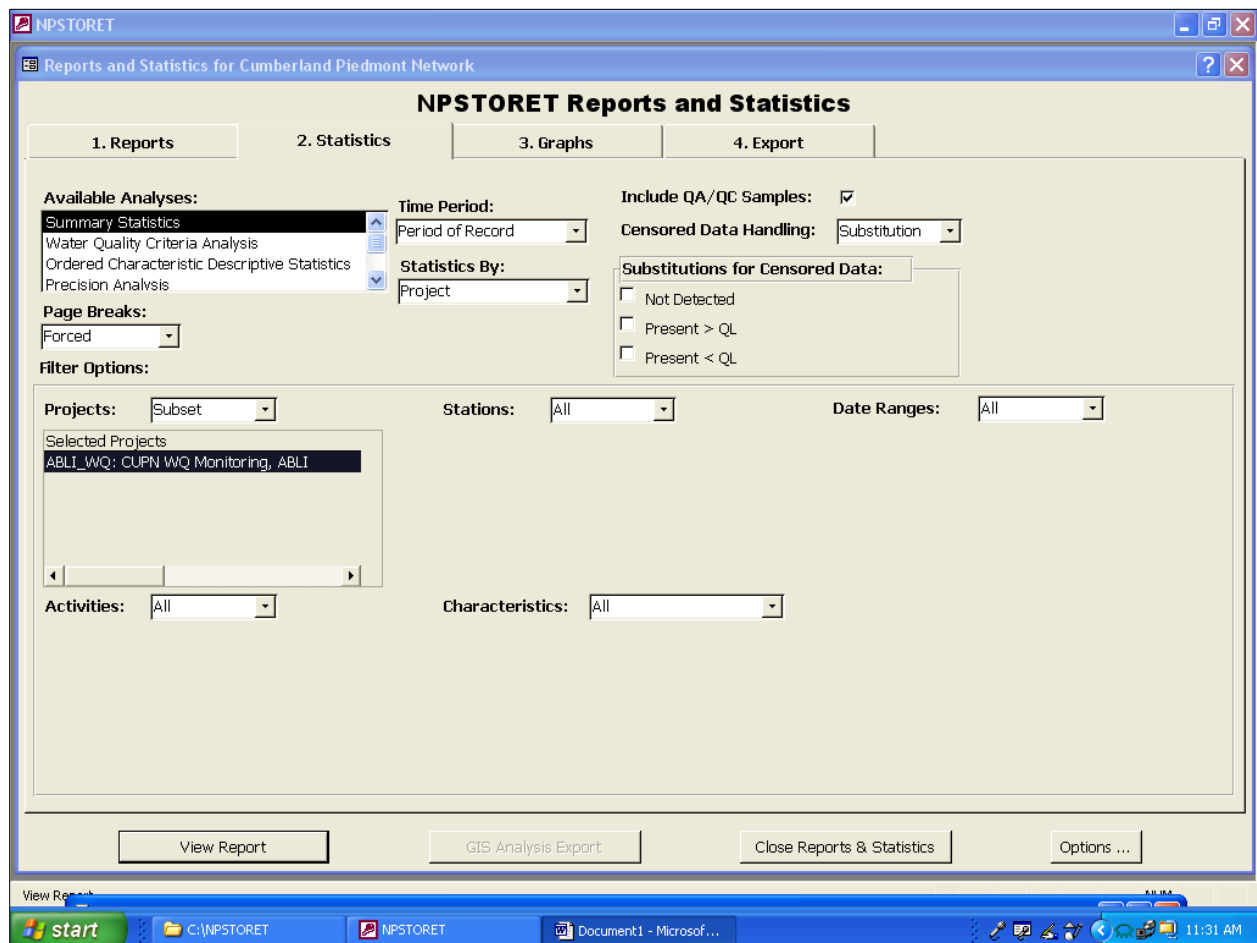


Figure SOP6-2. Screenshot of generating a descriptive statistics report in NPStoret.

1. Export Data to Microsoft Excel
 - a. Press the fourth tab, “Export.”
 - b. Select “Project” subset to the park in question.
 - c. Choose the “File Name” applicable to the project in question. File name must follow the format of park ID and date of validation; e.g., ABLI 01-25-2006.xls.

- d. Make sure that the “Fields” are a “subset” and contain the following selections:
 - i. Station ID
 - ii. Visit Start Date
 - iii. QA/QC Sample
 - iv. Local Characteristic Name
 - v. Result
 - vi. Other selections (see Figure SOP6-3)
- e. Press “Export Data.”
- f. Review the Microsoft Excel spreadsheet to find “out of range data.”

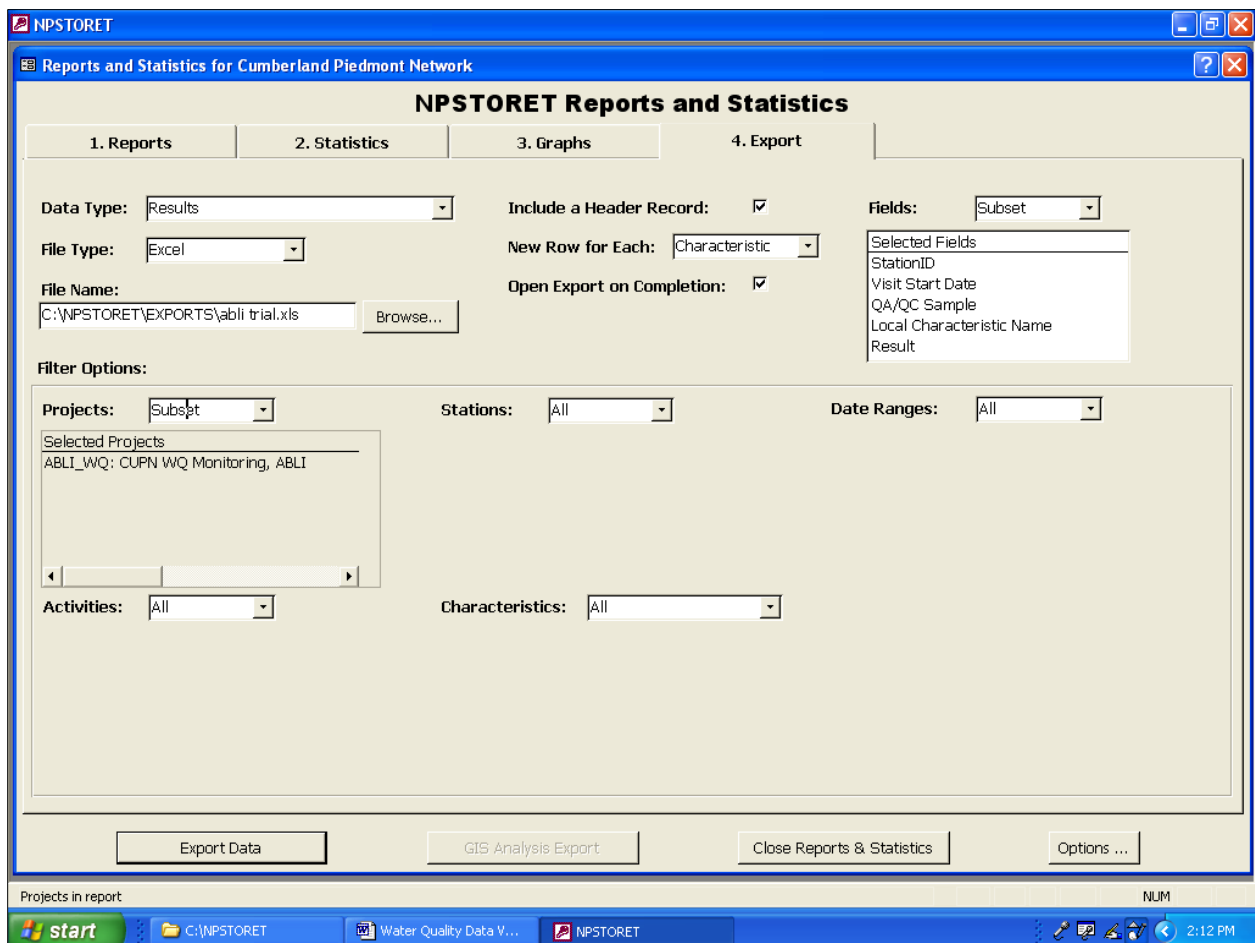


Figure SOP6-3. Screenshot of exporting data to Microsoft Excel in NPStoret.

2. Reporting Out-of-Range Data

- a. While still in the Microsoft Excel spreadsheet, create (insert) a new worksheet and label it “Corrections.”
 - b. Find and copy the entire row of out-of-range data to the “Corrections” worksheet.
 - c. In column “F,” make data correction notes for the data manager. These notes will instruct the data manager on exactly what corrective actions to take.
 - d. Save this spreadsheet in the NPStoret “Exports” “Data Validation” directory with the following naming protocol, consisting of the four-digit park name and date of validation event. For example, GUCO09-18-2007.
 - e. Place a note in the data manager’s file of activities.
3. Data Correction (Data Manager)
 - a. The data manager opens the Microsoft Excel files as noted by the validator and makes corrections in NPStoret.
 - b. The data manager then makes notes about the action taken in column “G” of the Microsoft Excel spreadsheet.
 - c. The spreadsheet is re-saved with original file name, as above (Step C4).
4. Iterations
 - o Since this process may only catch the single-most highest or lowest out-of-range data point, each project should be re-validated to assure additional out-of-range data points do not exist. The hydrologist should take care when scanning the Microsoft Excel spreadsheet to catch as many points as possible.
 - o The hydrologist moves each validated Microsoft Excel spreadsheet into the folder C:\NPSTORET\Exports\For DA Review.
 - o The data manager makes corrections and adds a seventh column in the “corrections” worksheet describing any action taken, per data entry. The data manager then moves this updated excel file into the folder C:\NPSTORET\Exports\DA Reviewed.
5. Documentation
 - a. The hydrologist and the data manager must keep a concise log and dialogue of data activities. Any time the hydrologist or the data manager performs a verification or validation process, the activity will be documented in a dialogue file.
 - b. The dialogue file will be used as a communication and record-keeping tool. For example, if the validator processed three files, this activity will be annotated in the

dialogue file and an email will be sent to the data manager telling them to look at the dialogue file for data updates. An email will only be sent if action is required. Each entry will be accompanied by the date of entry.

- c. Any data verification activities will also be documented in the dialogue file.
- d. The hydrologist keeps records in the Microsoft Excel file “Validation log.xls” in the folder C:\NPSTORET\Exports. When the hydrologist is satisfied that a particular park (project) is valid for the period of record, the date of final data validation is recorded in this spreadsheet.
- e. Similarly, the data manager will record data verification in the file “Verification log.xls” in the folder C:\NPSTORET\Exports.

Data Documentation

Final verified data sets will be documented with metadata using [Dataset Catalog \(v.3\)](#), developed by the WASO I&M office. Metadata will accompany all archived annual data sets on the CUPN server and distributed with data requests.

Data Dissemination

The ultimate goal of NPStoret is to make water-quality data available to park managers via data requests to responsible offices, and to the public at large via U.S. EPA STORET. The NPS Water Resources Division, after the annual CUPN water-quality data rollup, uploads these data into STORET where they are available to the public.

There may be various times throughout the year where individual parks, researchers or cooperators may request water-quality data from the Cumberland Piedmont Network. These requests are administered by the CUPN data manager. All data must undergo documented verification and validation procedures detailed in this SOP and contain metadata prior to release.

Data Maintenance, Storage, and Archiving

The Cumberland Piedmont Network has the master NPStoret data file, located on the network’s data server. The master version contains all years of data for the network. The working data file, also on the data server, is a new, empty file designated for the new year’s sampling data and is created annually by the data manager.

After all new data for the sampling year has been added to the working data file and data has been verified and validated, it will be sent to the Water Resources Division for further verification by the WRD data manager. If it meets their standards, the Water Resources Division will archive the data set internally and also send data specific to EPA STORET for inclusion in the National Data Warehouse (Figure SOP6-4). In addition, the Cumberland Piedmont Network will add the verified

and validated WRD-approved working data file to the master data file and archive it to a CD and tape back-up. This action will be repeated for every annual sampling event.

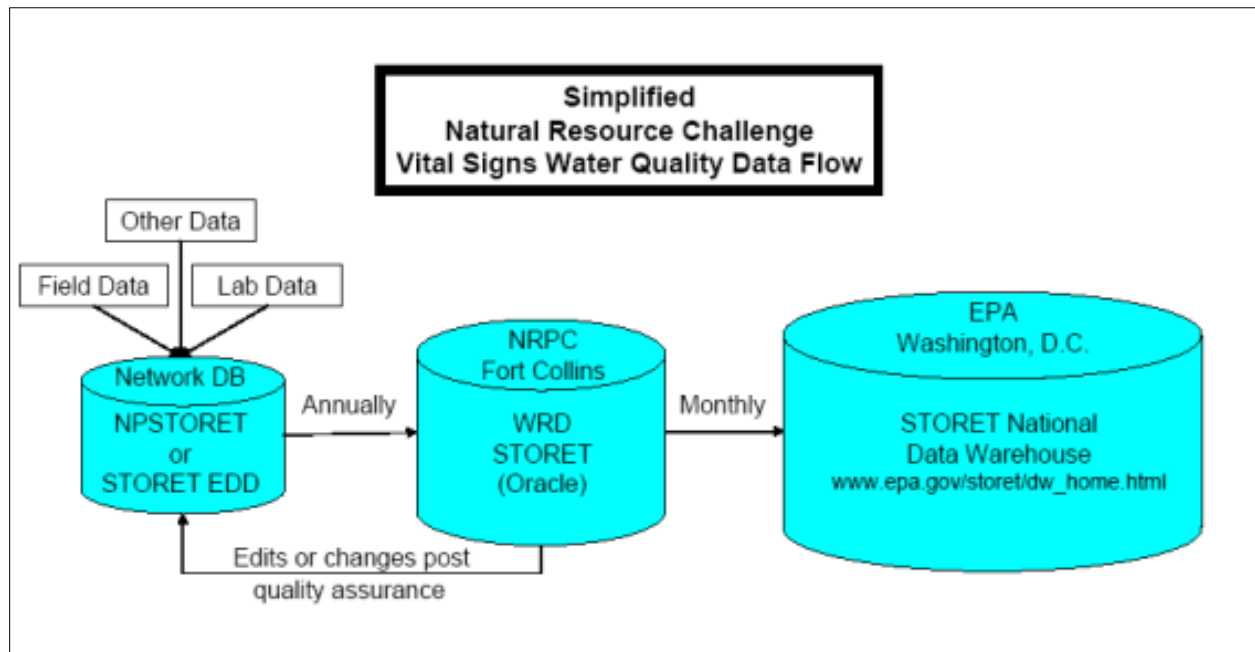


Figure SOP6-4. Simplified Natural Resource Challenge Vital Signs Water Quality Data Flow (from NPS 2015).

Literature Cited

National Park Service (NPS). 2015. Vital signs water quality data management and archiving.

Available at <https://www.nature.nps.gov/water/vitalsigns/vitalsignsmgt.cfm> (last accessed August 2017).

National Park Service Water Resources Division (WRD). 2016. Available at:

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Cumberland Piedmont Network

National Park Service
Inventory and Monitoring Division



Water Quality Monitoring Standard Operating Procedure 7

Data Analysis and Reporting—Version 1.2

Summary

This standard operating procedure (SOP) explains the steps involved in analysis of data collected during water-quality sampling in the Cumberland Piedmont Network (CUPN). It also explains the steps involved in reporting data from water-quality sampling in the Cumberland Piedmont Network (CUPN).

Revision Log

New Version #	Date	Author	Changes Made	Reason for Change
1.1	12/9/2005	Joe Meiman	Trend analysis discussion	Consideration of new trend analysis
1.2	3/3/2017	Joe Meiman	Made data analysis part of protocol objectives	To be sure data analysis is reflected in program objectives
1.2	5/2/2017	Editor	Editorial review, format update	Protocol publication
1.2	8/22/2017	Editor	Combined SOP 7 and 8	Ease of use

Introduction

Park managers must keep in mind the water-quality monitoring program is designed to track long-term water-quality trends. That is, while sample collectors routinely take water samples and thus generate water-quality data, it will take several years of repeated sampling for a true picture of a park's water quality to emerge. The main measurement objective of the CUPN water-quality protocol is:

Determine status and trends in pH, specific conductivity, dissolved oxygen, water temperature, and *Escherichia coli* at all parks, plus acid neutralizing capacity, nitrate, and turbidity at selected parks.

This basic question will be answered as parks are sampled and re-sampled over the years. This water-quality program will provide park managers with a long-term data set. However, there may, in certain cases, be short-term answers to water-quality questions such as, "What is the condition of CUPN waters?" Acute violations of water-quality standards are brought to the attention of park managers via a trip report following each sampling event. The CUPN hydrologist is available, at the request of the park manager, to discuss these potentially short-lived degradations of water quality. Although such information is not included in statistical data analysis, it serves as an alert to park managers. On an intermediate scale, annual time-series graphs (explained later in this SOP) serve as an annual evaluation relative to state water-quality standards.

The crux of the program is in the main measurement objective posed above. It requires a long-term data set, on the scale of at least two complete sampling rounds. In lieu of an NPS national water-quality trend analysis approach, the Cumberland Piedmont Network is actively exploring options for a trend analysis most useful for park managers. Presently trend analysis methods from the National Atmospheric Deposition Program (NADP) (Figure SOP7-1) and data visualizers from the National Capital Region I&M Network (NCRN) are being considered.

In the NADP approach, a trend line is plotted for each parameter for each CUPN monitoring station. An average value is calculated for each bin (likely to be annual bins for quarterly and bi-monthly parks and seasonal bins for monthly parks). Criteria for acceptable data completeness is set at the 75% level per bin. The trend line is smoothed over a moving average (two to four bins) with a one-bin time step. Trend plots are automatically created from NPStoret export after each annual data certification.

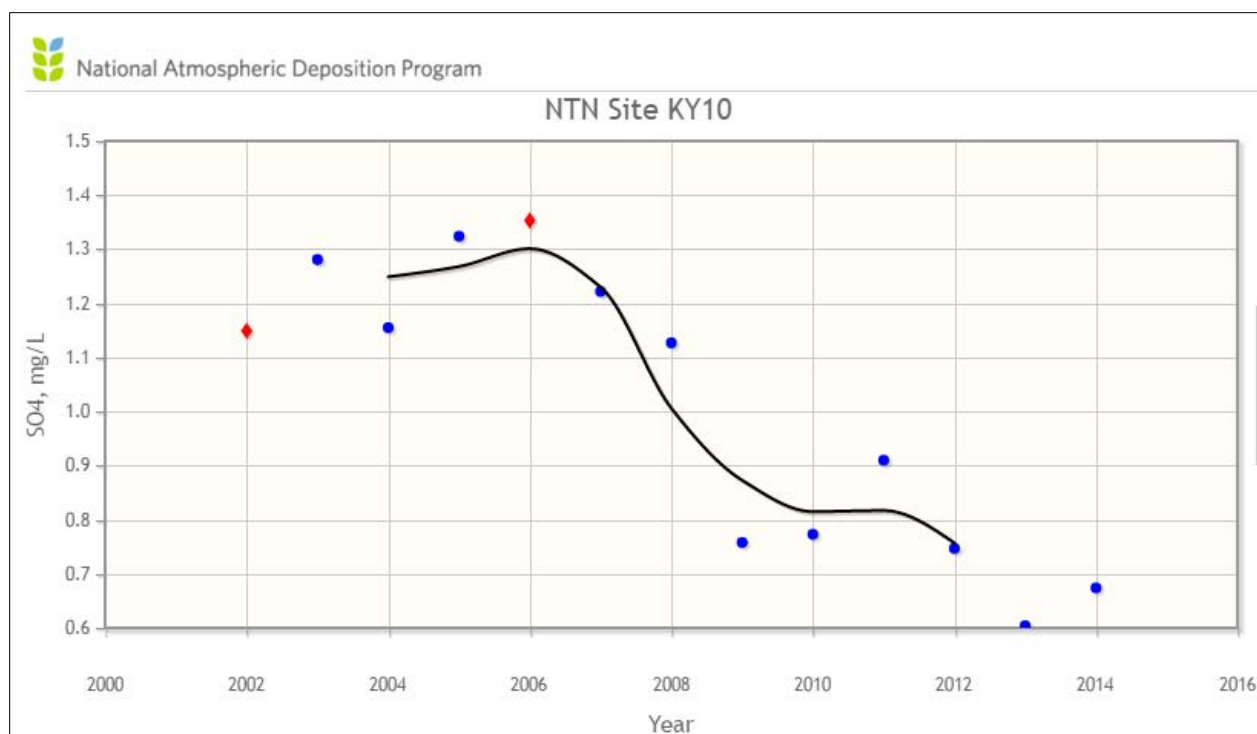


Figure SOP7-1. National Atmospheric Deposition Program trend plot of sulfate at the Mammoth Cave station (KY10). Red symbols indicate data did not meet criteria and are not used in trend calculation.

The National Capital Region Network has developed an “R” script and web site that performs a series of analyses. A test for seasonality is conducted, and if the results indicate seasonality then a sine curve is fitted to the data. If no seasonality is found a best fit regression line is applied. In both cases tests are conducted and reported for significant trends.

Field Reporting

It is the responsibility of the field sampler to complete all data entry, in both the field book and the water-quality (WQ) database, including all calculation fields (ANC and *E. coli*). The field sampler will send the electronic data and copies of the field book to the CUPN WQ data manager within three days of collection activities. The field sampler will also write a short narrative of the sampling activities and email it to the CUPN hydrologist, CUPN coordinator, and CUPN data manager, as well as the natural resources contact(s) at the sampled park. This narrative is also due within three days of the sampling event. The field sampler will assess supplies relative to the next scheduled sampling event. A list of needed supplies will be emailed to the hydrologist within a week of the conclusion of the sampling event.

CUPN Water-Quality Products

There are many ways to access CUPN Water-Quality Monitoring Program data. Each park has at least one detailed water-quality report available at the [CUPN website](#). While these reports provide a level of detail in both presentation and interpretation of results, they take time to produce. These reports remain valid and are an excellent reference of monitoring strategy and site descriptions; however, annual data products should provide resource managers with needed information briefly

and with rapid turnaround. At the end of each fiscal year, all WQ data entered in NPStoret will be sent to the National Park Service (NPS) Water Resources Division as part of the annual data roll-up. At this time, the CUPN hydrologist will prepared WQ reports for each park in which WQ monitoring was conducted during the year.

Water quality monitoring reports include the following products:

1. **Water Quality Resource Brief**—A simple synopsis of results from the year’s water-quality monitoring, including a list of state water-quality standards, a sample location map, overall water-quality status, an interpretation of water-quality standard violations (if any) and findings of interest, and a statement of the next scheduled water quality monitoring activity.
2. **Annual Water Quality Standards Analysis Report**—A list of water-quality violations for the concluded year for all water-quality parameters with assigned standards. This report displays the parameter, citation, units, number of observations, and number of times and percentage of times a specific standard was exceeded.

The following data products are available upon request:

1. **Water Quality Results, Data and Graphs**—Two Microsoft Excel worksheet files that summarize period-of-record results of each parameter for each sample location. The two files present the same data in two different graphic forms: time-series graphs and box-and-whisker plots.
2. **Full data export**—A Microsoft Excel file of all data and metadata for all sites and all parameters over the period of record.

Beginning in FY 2018 Water-Quality Trend Reports will be generated for each park active in water quality monitoring the previous fiscal year. Trend reports will consist of graphs similar to the example shown in Figure SOP 7-1. Trend graphs will be generated for each monitored parameter and display state water-quality limits for reference. Trend graphs will also predict when a particular parameter will exceed a state water-quality standard.

Cumberland Piedmont Network

National Park Service
Inventory and Monitoring Division



Water Quality Monitoring Standard Operating Procedure 8

Revising the Protocol—Version 1.2

This standard operating procedure (SOP) details the steps required to update and revise the CUPN water quality protocol (Meiman 2017) and related SOPs.

Revision Log

New Version #	Date	Author	Changes Made	Reason for Change
1.1	3/3/2017	Joe Meiman	Removed language that small changes can be approved by Network Coordinator and larger changes approved by the CUPN BOD.	Directly stated details for protocol revision.
1.2	5/1/2017	Editor	Editorial review, format update	Protocol publication
1.2	8/22/2017	Editor	Renumberd from SOP 9 to SOP 8	Combined original SOP 7 and SOP 8

Scope and Applicability

Due to the long-term nature of the CUPN monitoring program, revisions to the protocol narrative and to individual standard operating procedures (SOPs) will be necessary from time to time (O’Ney 2005). Careful documentation of changes to the narrative and its related SOPs, along with retaining a library of previous versions, is essential for maintaining consistency in the collection, summary, analysis, and reporting of data. The Revision History Logs found at the beginning of the narrative and each SOP list all edits to that section since the original publication date. Information entered in these logs should be complete and concise. The logs track the date of revision and new version number, author(s) of revision, description of change, and the reason the change was made.

Instructions for Recording Revisions

Protocol users must promptly notify the CUPN project leader about recommended or required changes. The CUPN project leader will then review and incorporate all changes, update the Revision History Log and change the date and version number on the title page of the master document as well as any SOPs the revisions apply to.

Minor Revisions

Minor revisions are those that *do not* represent a change in the underlying methods or procedures used to generate data values for the protocol’s existing data set. Minor revisions include small changes in, or clarification of, procedures. Version numbers for minor revisions increase incrementally by tenths (1.1, 1.2, 1.3...).

Major Revisions

Major revisions are those that involve changes in methodology that could influence the resulting data values and the ability to compare newly-collected data with data collected using a previous version, such as:

- addition of monitoring objectives;
- changes to the sampling design;
- changes to reporting requirements; or
- addition of new variables.

Major revisions are designated with the next whole number in the sequence (2.0, 3.0, 4.0...).

The CUPN project leader will also update all associated field forms to reflect the change in protocol version. Users noting discrepancies in versions between the protocol, SOPs, data values, and field forms should notify the CUPN project leader so that corrections can be made and documentation kept current.

Reviewing Suggested Protocol Revisions

All suggested edits require review by the CUPN project leader for clarity and technical soundness. Small changes or additions to existing methods will be reviewed by CUPN staff. However, if a significant change in methods is recommended, additional expert review may be required. All changes to the protocol will be subject to approval by the regional I&M coordinator.

Communicating Changes to Investigators/Users

Once changes have been made, the updated document is posted on the Integrated Resource Management Applications (IRMA) system under the Cumberland Piedmont Water-Quality Monitoring Project (National Park Service 2017). All previous versions are also available under the same project on IRMA. Each time an SOP is revised, the CUPN project leader ensures that all known users obtain a current copy of the SOP and receive the necessary briefing material and/or training to understand and incorporate the change(s). Anyone tasked with implementing the CUPN water-quality monitoring protocol will be contacted by the CUPN project leader before sampling or analyzing and reporting monitoring data to ensure the use of the most recent protocol and associated SOPs.

Literature Cited

- Meiman, J. 2018. Cumberland Piedmont Network water quality monitoring protocol: Version 2.0. Natural Resource Report NPS/CUPN/NRR—2018/1657. National Park Service, Fort Collins, Colorado.
- O’Ney, S.E. 2005. Standard operating procedure 11: Revising the protocol,—Version 1.0. *In*: O’Ney, S.E. 2005. Regulatory water quality monitoring protocol. Version 1.0. Bozeman (MT): National Park Service, Greater Yellowstone Network.
- National Park Service. 2017. Integrated Resource Management Applications, “Cumberland Piedmont Network Water Quality Monitoring Project.” Available at: <https://irma.nps.gov/DataStore/Reference/Profile/2238503> (last accessed August 2017).