

**NPDES DISCHARGE MONITORING COALITION
PROGRAM**

FIELD MONITORING GUIDANCE

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ECOSYSTEMS UNIT

TABLE OF CONTENTS

| | |
|--|-----------|
| LIST OF FIGURES | v |
| LIST OF TABLES | v |
| ACRONYMS/ABBREVIATIONS | vi |
| 1 SCOPE AND APPLICATION | 1 |
| 2 SAFETY | 2 |
| 3 WATER QUALITY SAMPLING OVERVIEW | 3 |
| 3.1 Sampling Location and Frequency | 3 |
| 3.1.1 Sampling Location | 3 |
| 3.1.2 Site Verification..... | 3 |
| 3.1.3 Trespassing..... | 4 |
| 3.1.4 Sampling Frequency | 4 |
| 3.1.5 Missed Samples | 4 |
| 3.2 Field Sampling Techniques | 5 |
| 3.2.1 Bank/Dock Sampling | 5 |
| 3.2.2 Field Parameter Measurement Technique | 5 |
| 3.2.3 Grab Samples | 6 |
| 3.2.3.a Grab Sampling Procedure — Direct Method | 7 |
| 3.2.3.b Grab Sampling — Intermediate Sampling Devices..... | 8 |
| 3.2.4 Photic Zone Sampling..... | 9 |
| 3.2.5 Secchi Depth Measurements | 10 |
| 3.3 Quality Control (QC) Samples | 11 |
| 4 FIELD PARAMETERS | 12 |
| 4.1 Field Parameter Measurements Overview | 12 |
| 4.1.1 DWQ Certification..... | 12 |
| 4.1.2 Field Instruments..... | 12 |
| 4.1.3 Field Meter Calibration..... | 12 |
| 4.1.4 Calibration Verification and Data Validation..... | 13 |
| 4.1.5 Field Meter Maintenance | 14 |
| 4.1.6 Backup Field Meters..... | 14 |
| 4.2 Temperature..... | 15 |
| 4.2.1 Annual Temperature Calibration Check..... | 15 |
| 4.2.2 Cleaning and Maintenance of Temperature Sensors | 15 |
| 4.3 Dissolved Oxygen (DO)..... | 15 |
| 4.3.1 DO Temperature Dependence | 15 |
| 4.3.2 DO Calibration in Water-Saturated Air..... | 15 |
| 4.3.3 DO Calibration Verification and Data Validation..... | 17 |
| 4.3.4 Secondary Checks for DO | 17 |
| 4.3.5 DO Maintenance and Troubleshooting..... | 18 |

| | | |
|----------|---|-----------|
| 4.4 | pH | 18 |
| 4.4.1 | pH Temperature Dependence | 18 |
| 4.4.2 | pH Calibration | 19 |
| 4.4.3 | pH Calibration Verification and Data Validation | 19 |
| 4.4.4 | pH Maintenance and Troubleshooting | 20 |
| 4.5 | Conductivity (Specific Conductivity at 25 °C) | 21 |
| 4.5.1 | Conductivity Temperature Dependence | 21 |
| 4.5.2 | Conductivity Calibration Standards | 21 |
| 4.5.3 | Conductivity Calibration..... | 21 |
| 4.5.4 | Conductivity Calibration Verification and Data Validation | 22 |
| 4.5.5 | Maintenance and Troubleshooting..... | 23 |
| 5 | SAMPLE COLLECTION AND PRESERVATION | 24 |
| 5.1 | General..... | 24 |
| 5.1.1 | Bottles and Preservation..... | 24 |
| 5.1.2 | Sample Documentation..... | 24 |
| 5.2 | Chlorophyll <i>a</i> | 25 |
| 5.3 | Conductivity (specific conductivity at 25 °C) | 25 |
| 5.4 | Fecal Coliform..... | 25 |
| 5.5 | Nutrients | 26 |
| 5.6 | Total Recoverable Metals..... | 26 |
| 5.7 | Suspended Residue | 28 |
| 5.8 | Turbidity..... | 28 |
| 6 | STANDARD CLEANING PROCEDURES | 29 |
| 6.1 | General Sampling Equipment | 29 |
| 6.2 | Labline Samplers | 29 |
| 6.3 | Field Meters..... | 29 |
| 6.4 | Coolers and Shipping Containers..... | 29 |
| 6.5 | Sampling Containers | 29 |
| 7 | DWQ FIELD VISITS AND QA/QC STUDIES | 30 |
| 7.1 | Field Visits | 30 |
| 7.2 | QA/QC Studies..... | 30 |
| 8 | REFERENCES AND HYPERLINKS | 31 |

APPENDICES

| | | |
|-------------|--|----|
| Appendix A. | Flagging Data taken Prior to Failed Calibration Verifications | 33 |
| Appendix B. | Data Remark Codes..... | 34 |
| Appendix C. | DWQ AMS Field Calibration Sheet | 37 |
| Appendix D. | DWQ AMS Dissolved Oxygen Solubility Table and Dissolved Oxygen Correction Chart..... | 38 |

Appendix E. Dissolved Oxygen Maintenance Tips and Details for Polarographic Probes..... 40
Appendix F. pH Maintenance Tips and Details 42
Appendix G. Conductivity Maintenance Tips and Details 43
Appendix H. Director’s Memo Regarding Metals Monitoring Suspension 44
Appendix I. NPDES Coalition Field Monitoring Checklist 47

LIST OF FIGURES

| | |
|---|-----------|
| Figure 1. Grab Sampling Bottle Orientation..... | 7 |
| Figure 2. Cage Sampler Used in the DWQ Ambient Monitoring System | 8 |
| Figure 3. Pole Sampler | 8 |
| Figure 4. Labline Sampler for Photic Zone Measurements..... | 9 |
| Figure 5. Secchi Depth Measurement | 10 |

LIST OF TABLES

| | |
|--|-----------|
| Table 1. Recommended Calibration Drift Acceptance Criteria..... | 13 |
| Table 2. Dissolved Oxygen Troubleshooting Table | 18 |
| Table 3. pH Troubleshooting Table | 20 |
| Table 4. Conductivity Troubleshooting Table..... | 23 |

ACRONYMNS/ABBREVIATIONS

| | |
|------------------|---|
| 40 CFR 136 | Code of Federal Regulations, Title 40, Part 136 |
| AMS | Ambient Monitoring System |
| ATC | Automatic Temperature Compensation |
| DENR | Department of Environment and Natural Resources |
| DO | Dissolved Oxygen |
| DWQ | Division of Water Quality |
| EPA | Environmental Protection Agency |
| GPS | Global Positioning System |
| MOA | Memorandum of Agreement |
| MSDS | Material Safety Data Sheet |
| NPDES | National Pollutant Discharge Elimination System |
| NIST | National Institute of Standards and Technology |
| QA | Quality Assurance |
| QA/QC | Quality Assurance/Quality Control |
| QC | Quality Control |
| SM | Standard Methods |
| SOP | Standard Operating Procedure |
| TKN | Total Kjeldahl Nitrogen |
| TP | Total Phosphorus |
| USGS | United States Geological Survey |

1 SCOPE AND APPLICATION

This document provides guidance for the collection of field data and laboratory samples for the North Carolina NPDES Discharge Monitoring Coalition Program (“coalition program”). Data reported under the coalition program are potentially useful in many areas of water quality management and decision-making, including watershed assessments, modeling, and permit writing. The purpose of this document is to offer general guidelines to provide consistency, improve data quality, and maximize the usability of the data collected under the coalition program for multiple areas of water quality assessment and management.

The Memorandums of Agreement (MOA) between each coalition and the DWQ specify that sample collection for the coalitions shall be performed by trained personnel using the DENR DWQ Standard Operating Procedures Manual, Physical and Chemical Monitoring (February 1996) or subsequent documents as guidance. This document has been customized to meet the specific needs of the coalition program. These guidelines are intended to supplement the requirements and recommendations of the DWQ Wastewater/Groundwater Certification Branch as well as to recommend pertinent practices employed by the DWQ Ambient Monitoring System (AMS). In the cases where the techniques of the AMS exceed the requirements of the DWQ Certification Branch, the AMS techniques are highly recommended in order to ensure comparability between coalition and DWQ data.

Each coalition has the responsibility of managing the collection, analysis, and submittal of data as described in its MOA. All field analyses and laboratory analyses must be performed by a DWQ Wastewater/Groundwater certified laboratory. Any contract laboratory hired by the coalitions to meet the MOA requirements will have their own standard operating procedures (SOP). This guidance document is intended to help provide data that is comparable to DWQ data. Consistency with DWQ data enables the coalition data to be used comparably for water quality management and decision-making. Inconsistencies from DWQ techniques may prevent the application of the coalition data in certain water quality management decisions. Sampling methods and techniques not described in this document may be negotiated if they meet the requirements of the MOA, the DWQ Wastewater/Groundwater Certification Branch, and 40 CFR 136. Approval by DWQ of any negotiated methods will be documented in writing.

The rules and regulations of the Wastewater/Groundwater Laboratory Certification Branch have primacy over this guidance document. In the event any discrepancies are noted, follow the requirements of the Certification Branch and notify the DWQ coalition coordinators so that the discrepancy may be addressed.

Mention of trade names or commercial products in this document does not constitute endorsement or recommendation for use by the North Carolina Division of Water Quality.

2 SAFETY

Safety should be a primary concern when monitoring for the coalition program. Laboratories conducting water quality monitoring are encouraged to document their safety practices and guidelines.

Recommended safety practices include:

- Be aware of surrounding conditions; traffic, weather conditions, bank stability, and environmental issues (plants, bugs, etc.) can result in unsafe conditions. Take appropriate precautions.
- Park in a safe location, preferably where flashers will warn oncoming traffic. Flashing beacons and/or vehicle strobes as well as parking brakes improve safety while parked on the roadside.
- Monitors are advised to wear a safety vest during the entire sampling event.
- Sampling on a boat should only be conducted with at least two people present. Monitors are encouraged to wear personal floatation devices at all times while on the boat.
- Store chemicals in a safe, secure manner. Monitors are encouraged to wear safety glasses and gloves when handling chemicals. The material safety data sheet (MSDS) of each reagent describes appropriate storage and disposal instructions for used chemicals.
- If a monitor or other project staff feels a station is unsafe, they should notify the coalition coordinator and alternate locations will be assessed.

3 WATER QUALITY SAMPLING OVERVIEW

The purpose of collecting water quality samples is to obtain a representative portion of the water body being evaluated. Proper sampling procedures cannot be overemphasized.

Valid results and interpretations of the collected data depend on:

- Collecting representative samples;
- Employing proper sampling, handling, and preservation techniques;
- Properly identifying the collected samples and documenting their collection in permanent field records;
- Maintaining the integrity of all collected samples by properly packing and transporting them to the appropriate laboratory for analysis.

3.1 SAMPLING LOCATION AND FREQUENCY

3.1.1 Sampling Location

Monitoring locations are fixed stations (specific latitude/longitude). The MOAs describe the latitude, longitude, site location, and sampling frequency for each location. The stations have been selected to obtain the most representative stream sample. Generally, field monitors should make all reasonable attempts to:

- Conduct sampling and monitoring as consistently as possible at the same location in order to reduce unknown sources of variation.
- Sample in the main stream channel in an area of well-mixed flow outside of any discharge mixing zones.
- Take field parameter measurements and grab samples at the same location.
- Sample on the upstream side of bridges, boat docks, or other structures to avoid introducing contaminants that may be contributed by the structure.
- Site conditions may require that sampling occur from the bank or a boat dock. Follow the bank/dock sampling guidelines described in Section 3.2.1.
- Make a notation for any sites that are routinely sampled from the bank or downstream side of a bridge so that all monitors will sample from the same location.
- Safety concerns, accessibility, and stream flow patterns may temporarily force the monitor to collect samples on the downstream side of a bridge, from the bank, or from another slightly modified sampling location. Document these temporary changes on the field sheet and in the comments section of the monthly data submittal sheet.
- If for any reason sampling is prevented or if a change in location is required, it is expected that the monitor, laboratory, or coalition will inform a DWQ coalition coordinator within one week and make a notation in the comments section of the monthly data submittal sheet.

3.1.2 Site Verification

At least once per year, record GPS coordinates at each site in decimal degrees to at least the fourth decimal place. Verify the GPS coordinates against the most recent DWQ

coordinate verification (provided by the coalition coordinators). On their first site visit, new monitors are expected to confirm the field coordinates at each sampling location with a GPS device. GPS coordinates are expected to match the DWQ field verification coordinates to at least the first three decimal places. Greater variations in the fourth decimal place may be observed at larger rivers.

3.1.3 Trespassing

No trespassing on private property is permitted when accessing coalition program sampling sites. To date, permission to sample has been obtained for each coalition station located on private property. Any new sites established on private property will require gaining permission from the property owner. If at any time permission to access private land is denied or access is blocked, the coalition must cease sampling and notify the coalition coordinators. If access to a site requires parking in a private driveway, the monitor must obtain permission from the property owner.

3.1.4 Sampling Frequency

Sample in accordance with the schedule described in each MOA. DWQ expects that twice monthly sampling include a ten-day interval between monitoring events. This provides a better representation of water quality changes that may occur during the month. For instance, if the first monitoring event of the month occurs on June 5th, the second monthly sample should not be collected until June 15th at the earliest.

3.1.5 Missed Samples

Every reasonable attempt should be made to sample in accordance with the schedule of the MOA. Sampling may be temporarily prevented at times due to site inaccessibility (flooding, bad weather, road construction, etc.), drought, instrument failure, or other unforeseen events. In these cases, the monitor is expected to notify the coalition coordinator within one week and to note the missed sampling event and justification in the comments section of the monthly data submittal sheet. A few specific scenarios are covered below:

- In the case of instrument failure, it is expected that the monitor will have backup equipment or will return to sample as soon as possible. Instrument failure is not an acceptable reason for missing a monthly sampling event
- If the sampling event is prevented due to a long term disturbance, such as bridge construction, DWQ will determine if site relocation is necessary.
- Sampling may be prevented due to dry stream conditions. Sampling may be temporarily suspended when the stream bed consists of stagnant, disconnected pools of water with no observable hydrological connection or when there is not enough volume in the stream to sample without collecting bottom sediment and/or surface scum. The monthly data submittal sheet must include the date, station number, and comment "dry stream". If the sample is collected under extremely low flow conditions, it is recommended that a comment be made in the comments section of the monthly data submittal sheets.

3.2 FIELD SAMPLING TECHNIQUES

3.2.1 Bank/Dock Sampling

Although sampling on the upstream side at bridge locations is preferred, field parameter measurements and sample collection must sometimes occur from the streambank or boat dock. Bank and dock sampling require special considerations in order to obtain field parameter measurements and water samples from the main stream flow. An extension pole, wading, or a combination of wading with an extension pole may be required. Perform dock sampling on the end of the dock on the upstream side.

Extension Pole: An extension pole allows the field probe and/or sampling bottle to reach as far into the center of the main flow as possible. When collecting samples, orient the pole sampler so that the mouth of the collection bottle faces upstream. Submerge the mouth of the bottle downward so as to avoid collecting surface scum.

Wading: Enter downstream of the sampling location and wade upstream. Disturb the sediment as little as possible, especially in slow moving waters or in areas of fine sediment. Samples must be collected on the upstream side of the monitor. An extension pole may be needed when wading to extend the sampling bottle to reach midstream conditions.

3.2.2 Field Parameter Measurement Technique

Field parameters are generally measured directly in the water with an electronic meter. This section describes general guidelines when using field meters to take field parameter measurements. Information regarding field meter calibration, calibration verification, data validation and reporting, and maintenance is described in Section 4.

Field parameters monitored under the coalition program include:

- conductivity (specific conductivity at 25 °C in $\mu\text{S}/\text{cm}$)
- dissolved oxygen (DO, reported in mg/L)
- pH (SU)
- temperature (°C)

Temperature must be analyzed immediately. Dissolved oxygen and pH must be measured within 15 minutes of sample collection, but it is strongly recommended that these be analyzed directly in the stream. Conductivity has a holding time of 28 days, therefore, it may be measured in the field or a sample may be collected for lab analysis (Section 5.3). Generally, it is preferred to measure these four field parameters directly in the stream.

Observe the following guidelines for field parameter measurements:

- Calibrate the meter prior to each sampling run following the guidelines in Section 4.
- In general, submerge probes approximately 0.15 m (6 in) below the surface. Do not allow the probe to disturb the sediment or lay on the stream bottom.

- Ambient light must be great enough to visibly observe the location of the probe and stream conditions. If sampling under low light conditions, such as near dawn or dusk, use supplemental lights (flashlights, etc.) in order to observe the location of the probe.
- Ensure flow is sufficient for making accurate dissolved oxygen readings. The amount of flow required is instrument specific, but generally requires a circulator, manual stirring at a rate of 1 foot/second, or a probe engineered with reduced stirring dependence.
- After submersion of the probes, wait for readings to stabilize (typically at least one minute).
- Confirm any unusual readings by checking the probe in a standard that will bracket the field reading. pH 2 or 12 buffer may be needed for extreme situations. For instance, when monitoring in certain swamp waters that frequently have pH readings less than 4, it is wise to confirm the pH probe response in pH 2 buffer.
- Mid-day calibration verifications are strongly recommended.
- Final calibration verifications for each parameter (Section 4.1.4) must be performed at the end of the sampling run to verify the meter did not drift out of acceptable calibration limits.

3.2.3 Grab Samples

Grab samples are used to characterize the medium at a particular point in time. All grab samples shall be taken at approximately 0.15 m (6 in) below the surface unless otherwise requested. Collect grab samples in the same location where field parameters are made. This should be in a region of well-mixed flow, as described in Section 3.1.1. It is recommended that monitors wear a new pair of disposable laboratory gloves at each site for personal safety and to avoid contamination of the samples.

The following parameters are taken as grab samples in the coalition program, unless otherwise specified:

- Fecal coliform
- Metals: aluminum (Al), arsenic (As), cadmium (Cd), copper (Cu), chromium (Cr), iron (Fe), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), zinc (Zn)
- Nutrients: ammonia (NH₃); total kjeldahl nitrogen (TKN); nitrate/nitrite (NO₃+NO₂); total phosphorus (TP)

NOTE: *At sites where chlorophyll a is collected as a photic zone sample, nutrients are also to be collected as a photic zone sample. At sites where chlorophyll a is sampled in summer months only, nutrients are to be collected as a photic zone sample year-round.*

- Suspended residue (a.k.a. total suspended solids (TSS))
- Turbidity

3.2.3.a Grab Sampling Procedure — Direct Method

- 1.) Always ensure bottle labels match the sampling site location.
- 2.) Remove the cap from the bottle just before sampling.
NOTE: *Protect the bottle from contamination. Avoid touching the inside of the bottle or cap. If the inside of the bottle is touched, use another one. If the caps must be set down, place so that the inside of the lid faces upwards.*
- 3.) Plunge the bottle into the water with the mouth facing downward and pointing upstream while avoiding surface scum (Figure 1). The mouth should also be oriented away from the hand of the collector, the shore, the side of the sampling platform, or the boat.

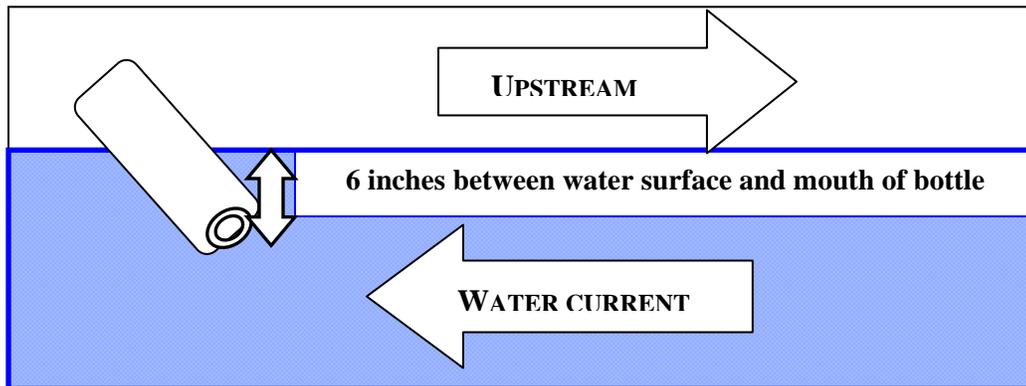


Figure 1. Grab Sampling Bottle Orientation

- 4.) Once underwater, tip the bottle slightly upwards to allow air to exit and the bottle to fill. The mouth of the bottle should be approximately 0.15 m (6 in) below the water surface.
- 5.) Once full, recap the bottle. Unless otherwise specified by the analytical laboratory, leave a small headspace. This allows the sample to be shaken prior to analysis.
- 6.) Add preservatives if needed.
- 7.) Ensure the bottle is labeled appropriately. Check that the following information is correct: site location, date, time, collector, parameter(s), and preservative(s).
- 8.) Place bottles in cooler within 15 minutes for transport to the lab. Follow guidelines in Section 5.1.1 regarding storage of samples on ice.

3.2.3.b Grab Sampling — Intermediate Sampling Devices

Sampling from bridges may require the use of an intermediate sampling device. Intermediate sampling devices include cage samplers (Figure 2), pole samplers (Figure 3), weighted bottle frames, and similar custom-made devices. Custom-made sampling devices should be evaluated by the DWQ coalition coordinators. The container employed as the intermediate sampling device should be constructed so that it meets the needs of the parameter (s) to be investigated.



Figure 2. Cage sampler used in the DWQ Ambient Monitoring System



Figure 3. Pole sampler

Grab Sampling Intermediate Devices Technique:

- 1.) Always ensure bottle labels match the sampling site.
- 2.) Place the bottle(s) securely in the intermediate sampling device. Confirm that each bottle is held securely.
- 3.) Remove the bottle cap(s) and lower the device to the water.
NOTE: *Protect the inside of the bottle from contamination. Avoid touching the inside of the bottle or cap. If the inside of the bottle is touched, use another one. If the caps must be set down, place so that the inside of the lid faces upwards.*
- 4.) Swing the sampling device downstream and then allow it to drop into the water while pulling on the rope so as to position the bottle openings upstream. Take care not to disturb the bottom sediment.
- 5.) Allow bottle(s) to fill.
- 6.) Pull the sampling device out of the water.
- 7.) Take care not to dislodge dirt or other material from the sampling platform.
- 8.) Unless otherwise specified by the analytical laboratory, leave a small headspace. This allows the sample to be shaken prior to analysis.
- 9.) Add preservatives if needed.
- 10.) Recap the bottle(s), remembering not to touch the inside of the bottle or cap.
- 11.) Ensure each bottle is labeled appropriately. Check that the following information is correct: site location, date, time, collector, parameter(s), and preservative.
- 12.) Place bottles in cooler within 15 minutes for transport to the lab. Follow guidelines in Section 5.1.1 regarding storage of samples on ice.

3.2.4 Photic Zone Sampling

Photic zone samples are vertical spatial composite samples (a.k.a depth-integrated composite samples) taken over the depth of the photic zone. The photic zone is defined by DWQ as twice the Secchi depth (described in Section 3.2.5). Photic zone samples are collected by lowering an integrated depth-sampling device, such as a Labline® sampler (Figure 4) to twice the Secchi depth and then slowly raising the device to the surface to obtain a representative water sample. The sampler is raised and lowered at a slow, constant pace throughout the region of twice Secchi depth until the sampler is full.

Photic zone samples are collected for:

- Chlorophyll *a* samples (at designated sites, assuming adequate water depth)
- Nutrients (to be collected as photic zone samples at sites where chlorophyll *a* is collected as photic zone samples. Nutrients should be collected year round as photic zone samples even when chlorophyll *a* is collected in the summer months only)

Photic Zone Sampling Technique

To collect a vertical spatial composite sample in the photic zone:

- 1.) Measure and record the Secchi depth (See Section 3.2.5.)
- 2.) Prior to collecting sample for analysis, rinse the integrated sampling device (Labline®) with sample water:
 - a. Lower Labline to the water. Take care not to disturb sediment.
 - b. Fill the Labline with water from the photic zone.
 - c. Raise to surface, swirl, and pour out water. Pour water away from sampling location so that the rinse water will not disturb the sample.

After rinsing, collect the sample for analysis:

- 3.) Lower the Labline to twice the Secchi depth. (i.e. if the Secchi depth is 0.5 m, lower the Labline so that the fill hole on the sampler is at 1 m depth).
- 4.) Raise the sampler to the surface at a slow, constant rate so as to collect a representative sample of the water column in the photic zone.
- 5.) Continue to lower and raise the Labline throughout the photic zone in a slow, constant motion until the sampler is full. Maintain a steady pace so as to ensure a representative sample.
- 6.) Pour sample from Labline into appropriate sample bottle.
NOTE: *Chlorophyll a sample bottles must protect the sample from light. Brown opaque bottles are commonly used.*
- 7.) Rinse Labline thoroughly with distilled water after using to clean between sites.
NOTE: *Directions for cleaning the Labline® are found in Section 6.2.*



Figure 4. Labline sampler for photic zone measurements.

3.2.5 Secchi Depth Measurements

A Secchi disk with alternating black and white quadrants is used to measure water clarity (Figure 5). The disk is lowered into the water until it is no longer visible. The disk is then raised until it reappears. The Secchi depth is the average of the depths at which the disk vanished and reappeared.

Secchi depth measurements are used to:

- determine the photic zone depth
- quantify water clarity and to give a general indication of problems with algae, zooplankton, water color and silt

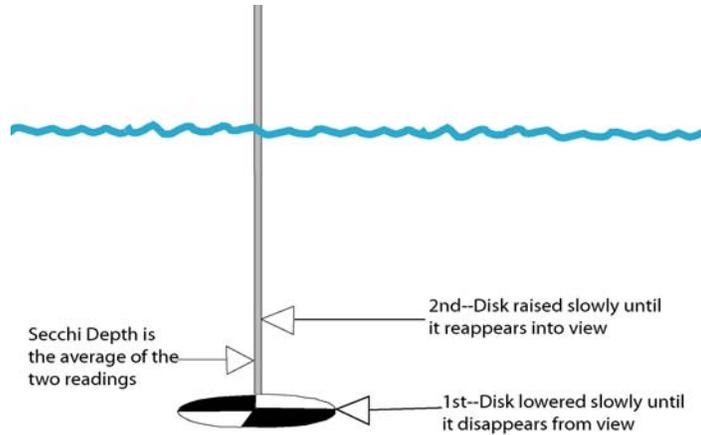


Figure 5. Secchi depth measurement.

Secchi Depth Measurement Technique

- 1.) Attach the Secchi disk to a rope or steel rod accurately graduated in tenth meter increments.
NOTE: *Verification of rope graduation against a meter stick is necessary as rope will shrink or stretch with continued use. Verify at least once quarterly.*
- 2.) Position yourself with the sun at your back, on the shaded side of a vessel, bridge or dock. Do not wear sunglasses.
- 3.) Slowly lower the Secchi disk into water until it just disappears.
- 4.) Read the depth at which it disappeared from the marked line
- 5.) Raise the Secchi disk until it re-appears.
- 6.) Read the re-appearance depth from the marked line
- 7.) Take the average of the two readings to get the limit of visibility.
- 8.) Record the average reading on field sheet as Secchi depth reading to the nearest tenth of a meter.

TIP: *In waters with strong current, the use of a steel rod rather than a rope is recommended. An extra weight may need to be applied to the disk so that it remains flat and level under water.*

Reporting Secchi Depth Measurements

Report the Secchi depth measurement in the comments section of the monthly data submittal sheet to the nearest tenth of a meter.

3.3 QUALITY CONTROL (QC) SAMPLES

Certain procedures or special studies may require the collection of QC samples. The need and types of QC samples will be discussed with and documented by the coalition coordinators. The definitions below are provided for clarity when discussing various QC samples.

Split Sample: A split sample is a sample that has been equally divided into two or more subsamples. If multiple samples must be collected from the stream in order to gather an adequate sample volume for the split, mix all samples into one container and add any preservatives required. Then, split the homogenized, preserved sample into subsamples. Split samples are normally used to estimate variability introduced during sample transportation, processing, and laboratory analysis.

Duplicate Sample: Duplicate samples are two or more samples collected simultaneously from the same source and under identical conditions into separate containers (i.e. two grab samples taken side-by-side into two discrete containers). Duplicate samples are normally used to measure the natural variability of the sampling medium as well as the precision of a method, monitor, and/or analyst.

Field Blank: Field blanks are used to determine whether contamination has been introduced during sampling, storage, transport, and lab analysis. Field blanks are prepared in the field by processing analyte-free water through each of the steps involved in sampling. Field blanks should be prepared before collecting and processing the environmental samples at the site. For instance, analyte-free water is taken into the field in a carboy and poured into a sample container, which is then capped and transported to the lab like all other samples. If the method calls for the addition of a preservative, this should be added to the field blank in the same manner as the other samples. Field blanks are submitted to the lab along with all other samples.

Trip Blank: Trip blanks are prepared in the lab. They are samples of analyte-free media collected in the same type of container as the environmental sample, transported from the laboratory to the sampling site, and returned to the laboratory unopened. A trip blank is used to determine if contamination occurred due to improper sample container cleaning, contaminated blank source water, or exposure to contaminants during sample storage or transport.

Temperature Blank: A temperature blank is a container of water that is shipped with field samples and is used to determine whether the samples have been adequately cooled during shipment and storage. Temperature blanks allow a representative temperature to be taken without the risk of contaminating the samples. One temperature blank should be used per cooler. Temperature blanks can be prepared at any time before or during field sampling activities. Infrared (IR) thermometers are increasingly being used to measure the sample temperature upon receipt rather than a temperature blank.

4 FIELD PARAMETERS

4.1 FIELD PARAMETER MEASUREMENTS OVERVIEW

Section 4 describes meter calibration, calibration verification, data validation and reporting, and meter maintenance details. Field parameters include:

- conductivity (specific conductivity at 25°C, reported in $\mu\text{S}/\text{cm}$ to the nearest whole number)
- dissolved oxygen (DO, reported in mg/L to the nearest tenth)
- pH (reported in SU to the nearest tenth)
- temperature (reported in °C to the nearest tenth)

NOTE: *Section 3.2.2 describes important techniques when using meters to collect field parameter data at the sampling location.*

4.1.1 DWQ Certification

Contract labs are required to be certified by the DWQ Wastewater/Groundwater Laboratory Certification Branch. Field parameters may be certified under either laboratory certification or field parameter certification. Laboratory certification (which includes mobile laboratory certification) enables a contract lab to make field parameter measurements in the lab or in the field. Laboratory certification requirements are generally more extensive than field parameter certification requirements. DWQ Wastewater/Groundwater Laboratory Certification rules are found in [15A NCAC 02H.0800](#).

4.1.2 Field Instruments

A wide array of instrumentation from numerous manufacturers is available for collecting field parameter data. As a result, detailed universal directions cannot be provided. Always follow the manufacturer's instructions for instrument calibration, use, maintenance, and storage. **The guidelines in this document are supplementary to and not a replacement for the manufacturer's directions.**

4.1.3 Field Meter Calibration

Meters must be calibrated prior to each sampling run for DO, pH, and conductivity. All calibration data must be recorded on a standardized calibration sheet. Recording pre and post-calibration data is strongly recommended as a good practice. Pre-calibration data that differs greatly from post-calibration data may be a useful indicator that a meter problem exists or is developing and may help to pinpoint the source of the problem. **EXAMPLE:** *An extremely low % DO saturation prior to calibration, such as 65%, often indicates the membrane on the DO probe needs to be changed. In some cases, a great variation in pre-calibration data from the expected calibration value may prevent calibration entirely. For instance, a YSI polarographic DO probe will generally not calibrate if it reads less than 50-60% saturation prior to calibration.*

4.1.4 Calibration Verification and Data Validation

In order to verify and validate the data for use in most water quality management decisions, a post-sampling calibration verification must be performed at the end of each sampling run to assess the extent of calibration drift for pH, conductivity, and DO. A mid-day calibration verification is strongly recommended. Additional calibration verifications may be needed if unusual or impossible readings are observed (i.e. pH reading of 17).

Calibration Verification Technique

To perform a calibration verification, follow the same steps in the calibration routine without recalibrating the meter. When the probe(s) are under stable calibration conditions, record the time and the meter readings. Compare the meter readings to the expected standard values. The difference between these readings is the calibration drift. In order to achieve consistency with DWQ programs and ensure the maximum usability of the data in water quality management areas, it is strongly recommended that the maximum amount of allowable drift is the same as the calibration drift acceptance criteria used by the DWQ AMS. These criteria are presented in Table 1. Re-calibration is required if the meter exceeds the maximum amount of allowable drift. If performing the calibration verification in more than one standard, check all standards before recalibrating.

Table 1. Recommended Calibration Drift Acceptance Criteria

| Parameter: | Maximum amount of acceptable drift used by DWQ AMS: | Comments: |
|-----------------------------------|--|---|
| pH | ± 0.2 pH units from pH buffer value | Strongly recommended; enables data to be used comparably to DWQ AMS Data. |
| Specific Conductivity (at 25 ° C) | ± 10% from standard value | Required by DWQ Certification Branch |
| Dissolved Oxygen (DO) | ± 0.5 mg/L from theoretical DO value (from DO solubility tables) | Strongly recommended; enables data to be used comparably to DWQ AMS Data. |

Calibration verification is necessary for determining whether the instrument was within acceptable calibration throughout period in which samples were analyzed. A failed calibration verification indicates that the initial calibration is no longer valid and the meter requires recalibration (assuming the calibration verification was performed properly). All samples taken between the calibration and the failed verification must be flagged with a data remark code of J12 (“the calibration verification did not meet the calibration acceptance criterion for field parameters”) and the extent of calibration drift documented in the comment column. For calibration verifications involving more than one standard, the data must be flagged if the verification fails in any of the standards. Appendix A contains an example data submittal utilizing the J12 remark code and calibration drift documentation. Appendix B presents the data remark codes used in DWQ programs. These codes can also be found on the

[Laboratory Section's Quality Assurance website](#). The DWQ AMS calibration/calibration verification sheet is presented in Appendix C for an example as to how DWQ incorporates calibration verifications into the DWQ calibration process.

The flagging of data with a “J12” and documentation of the calibration drift in the comments section will provide a high level of confidence when using the data, particularly in critical areas such as use assessment. The data verification procedure described in this document is designed to provide equitability with DWQ AMS field parameter data and to prevent the use of suspect or erroneous data in use support and impairment decisions. Alternative methods of data validation may be acceptable. In order to ensure the maximum level of data usability, alternative methods must be discussed with DWQ coalition coordinators and acceptance documented in writing.

4.1.5 Field Meter Maintenance

Regular maintenance must be performed on all meters. A maintenance log will reduce the occurrence of meter failure in the field, especially when multiple personnel use the same meter.

Common indicators that maintenance is needed:

- Meter will not calibrate
- Erratic, unstable readings
- Meter drifts quickly and frequently after calibration
- Meter repeatedly fails calibration verification
- Pre-calibration values differ greatly from standards
- Slow response time (the meter takes a long time to stabilize after the instrument is turned on and/or when submersing in sample)
- Probe condition is visibly compromised
- DO membrane is wrinkled, dry, or covered with biological growth
- Discolored spots on DO anode or cathode
- pH probe has film on it or reference junction is discolored
- Dirt/debris in conductivity cell
- Record of last maintenance is not available

4.1.6 Backup Field Meters

Meter failure is expected and may occur at anytime. Therefore, it is expected that personnel carry functional back-up meters, maintenance accessories, and batteries with them at all times. Meter failure is not an acceptable reason for the inability to collect monthly data.

4.2 TEMPERATURE

Immerse the temperature sensor in water long enough to reach equilibrium (as indicated by a stable temperature). Temperature stability will vary according to water circulation at the sampling site, but is typically within ± 0.5 °C. Report reading to 0.1 °C resolution.

4.2.1 Annual Temperature Calibration Check

NC Wastewater/Groundwater Laboratory Certification Branch Policy requires that all thermometers and temperature measuring devices be checked every 12 months against a NIST certified thermometer and the process documented. This requirement is described in the [Guidelines for Field Analysis of Temperature](#) document on the DWQ Certification Branch website. The serial number of the NIST thermometer or traceable thermometer that was used in the comparison must be documented. The thermometer/meter readings must be less than or equal to 1 °C from the NIST certified or NIST traceable thermometer reading. The temperature correction (even if it is zero) must be posted on the meter as well as in hard copy format.

4.2.2 Cleaning and Maintenance of Temperature Sensors

A dirty temperature sensor may cause erroneous readings. Refer to the manufacturer's instructions for cleaning and maintaining the temperature sensor.

4.3 DISSOLVED OXYGEN (DO)

DO calibration and maintenance guidelines included in this section are to be used as a supplement to the meter manufacturer guidelines and DWQ certification requirements and not as a replacement. Methods for calibration include using water-saturated air, air-saturated water, and Winkler titrations. Because water-saturated air is the most common method, it is the sole method described in these guidelines.

4.3.1 DO Temperature Dependence

DO is a temperature-dependent parameter; therefore, the temperature sensor must be working correctly and be submersed in solution. Temperature and DO values must be stable before calibrating.

Annual Temperature Verification for DO

DWQ Certification Branch Policy requires that the temperature sensor be verified every 12 months and the process documented. The DWQ Certification Branch outlines the procedure in the [Guidelines for Field Analysis of Dissolved Oxygen](#) document available on their website.

4.3.2 DO Calibration in Water-Saturated Air

Good practices for water-saturated air calibration are outlined below. These are intended to supplement the manufacturer's guidelines and not to be used as a replacement.

- Allow adequate time for the meter to stabilize under 100% water-saturated air conditions. This will be specified by the manufacturer. It is generally 5-15 minutes.
- Ensure the calibration chamber is vented to the atmosphere. It is critical that the pressure within the calibration cup be equal to the ambient atmospheric pressure.
- Ensure no water droplets are on the membrane or temperature sensor during a calibration or calibration verification. If water droplets are observed on the membrane, the water droplets must be removed (by blotting or shaking the probe) and the calibration or calibration verification process must be repeated.
NOTE: *This is a very common source of error in the DO calibration and calibration drift checks. Water droplets on the membrane typically produce low readings. Droplets on the temperature sensor cause temperature instability due to evaporation.*
- Ensure the temperature is stable (generally stable to within 0.5 °C).
- Obtain accurate barometric pressure or altitude for the calibration location. Know the barometric pressure or altitude for each sampling site in the event that the meter needs to be checked or recalibrated in the field.
- Record the barometric pressure or altitude used in the calibration.
- Record the following readings both before and after calibration:
 - Temperature
 - DO in mg/L
 - DO % saturation (recommended for quick troubleshooting)
- Use an oxygen solubility table to verify the meter calibrated to within 0.5 mg/L of the theoretical oxygen solubility for the corresponding barometric pressure (or altitude) and temperature. Do this by comparing the meter reading after calibration to the table value. Appendix D presents the oxygen solubility table used by the DWQ Ambient Monitoring System. Oxygen solubility tables can also be downloaded from the USGS website at:
<http://water.usgs.gov/software/dotables.html>

4.3.3 DO Calibration Verification and Data Validation

In order to validate the DO readings, a dissolved oxygen calibration verification must be performed at the end of a sampling run. A mid-day calibration verification is also strongly recommended.

A calibration verification follows the same steps in the calibration routine without recalibrating the meter. When the DO probe is under stable calibration conditions, record the following readings:

- Time
- DO readings in mg/L
- DO % saturation (recommended for quick troubleshooting)
- Altitude or barometric pressure at the site where the calibration verification is performed

Then, compare the meter reading to theoretical oxygen solubility values (Appendix D, <http://water.usgs.gov/software/dotables.html>). Use of the recommended ± 0.5 mg/L criteria will provide consistency with other DWQ programs. If the meter does not read within 0.5 mg/L of the theoretical value, recalibrate the meter. Flag data between an initial calibration and a failed calibration check with a remark code of J12 and document the extent of calibration drift in the comments section of the monthly data submittal sheets, as described in Section 4.1.4. Calibration Verification and Data Validation and as demonstrated in Appendix A.

4.3.4 Secondary Checks for DO

Checking DO readings

Secondary checks on DO readings include performing Winkler titrations or checking readings against another meter. These checks might be desired to evaluate or troubleshoot the calibration and calibration verification process. If a secondary check is performed, the results should be recorded on the field data sheet and submitted in the comments section of the monthly data submittals.

Winkler Titrations: The Winkler titration, is an excellent way to evaluate the performance of DO meters. The method is described in the Standard Methods for the Examination of Water and Wastewater (Standard Methods 4500-O B 18th, 19th, and 20th eds.).

Alternate Meter: A secondary meter may be used to confirm meter performance. When using two meters side by side, note that the comparability of the readings will be a combination of both the accuracy of the DO probe and the accuracy of the temperature probe on each meter.

4.3.5 DO Maintenance and Troubleshooting

Follow the manufacturer’s guidelines for maintenance and troubleshooting. Table 2 summarizes general recommendations for polarographic probes. Appendix E provides more detailed troubleshooting and maintenance tips.

Table 2. Dissolved Oxygen Troubleshooting

| Symptoms | |
|--|--|
| Unable to calibrate (error message during calibration) | |
| Unusual or erroneous readings | |
| Unstable readings | |
| Failed calibration drift check | |
| Potential DO problem | Solution |
| Damaged membrane | Replace membrane with proper membrane from manufacturer |
| Lack of electrolyte/old electrolyte | Use fresh electrolyte. Make sure electrolyte is not expired and is the appropriate solution for the probe |
| Fouled or damaged anode or cathode | Clean anode/cathode per manufacturer’s instructions |
| Improper calibration conditions | Calibrate or verify performance under proper calibration conditions, including: <ul style="list-style-type: none"> • 100% humidity • stable temperature • no water droplets on membrane or thermistor • correct barometric pressure/altitude • calibration cup vented to atmosphere |
| Improper measurement conditions | Use proper measurement techniques, including maintaining sufficient water movement across the probe face (typically 1 ft. per second) |

4.4 PH

The pH calibration and maintenance guidelines included in this section are to be used as a supplement to the meter manufacturer guidelines and DWQ Wastewater/Groundwater Certification Branch Rules and Policy and not as a replacement.

4.4.1 pH Temperature Dependence

pH is a temperature-dependent parameter; therefore, the temperature sensor must be working correctly and be submersed in solution. Temperature and pH values must be stable before calibrating. Check the manufacturer’s instructions regarding temperature compensation during calibration. To avoid temperature compensation errors during calibration, it is often preferred to calibrate pH at temperatures close to 25 °C, such as in a laboratory environment.

Annual Automatic Temperature Compensation Verification for pH

DWQ Certification Branch Policy requires that the temperature sensor and the internal Automatic Temperature Compensator (ATC) be verified every 12 months and the process documented. The DWQ Certification Branch outlines the procedure to verify the ATC in the [Guidelines for the Field Analysis of pH](#) document available on their website.

4.4.2 pH Calibration

Good practices for calibration are outlined below. These are intended to supplement the manufacturer's guidelines and not to be used as a replacement.

- It is generally recommended to calibrate in pH 7 buffer first. Then calibrate in additional buffers which bracket the anticipated sample values. A two-point calibration is required by the DWQ Certification Branch. A three-point calibration is recommended if samples values are anticipated to have a pH both above and below a pH of 7.
- Prior to calibration, rinse probe with a small amount of calibration buffer and discard rinse.
- Many manufacturers' instructions require that the temperature-corrected buffer value (provided on the stock bottle) be entered during calibration.
NOTE: *This becomes particularly important when using pH 10 buffers at temperatures other than 25 °C.*
- To avoid temperature compensation errors during calibration, it is often preferred to calibrate pH at temperatures close to 25 °C, such as in a laboratory environment.
- Ensure both pH and temperature sensor are fully submerged. Wait for both readings to stabilize before finalizing the calibration.
- Record both the pre and post-calibration pH and temperature readings on the calibration sheet.
- Ensure meter calibrates to within 0.1 SU of the buffer value.
- After the calibration is finalized, perform an immediate calibration verification in pH 7 buffer. This is required by the DWQ Certification Branch for field parameter certification. The meter must read the buffer within the accuracy of the meter to be acceptable.

4.4.3 pH Calibration Verification and Data Validation

In order to validate the pH readings for use in multiple areas of water quality management, a calibration verification must be performed at the end of a sampling run. A mid-day calibration verification is strongly recommended. It is highly recommended

that the verification be performed in a pH 7 buffer and another buffer which brackets the sample values. Verifying the pH calibration in 2 buffers will provide consistency with other DWQ programs and provide a higher level of confidence in the data.

To perform the check, follow the same steps in the calibration routine without recalibrating the meter. When the pH probe is under stable calibration conditions, record the following information in each buffer without recalibrating the meter.

- Time
- Buffer value
- Calibration check value

If the meter reading differs from any of the buffers by more than 0.2 SU, the meter must be recalibrated. Flag the data between the initial calibration and the failed calibration check with a remark code of J12 and document the extent of calibration drift in the comments section of the monthly data submittal sheets, as described in Section 4.1.4. Calibration Verification and Data Validation and as demonstrated in Appendix A.

4.4.4 pH Maintenance and Troubleshooting

Follow the manufacturer’s guidelines for maintenance and troubleshooting. Table 3 summarizes general recommendations. Appendix F provides more detailed troubleshooting and maintenance tips.

Table 3: pH Troubleshooting

| Symptoms | |
|--|--|
| Unable to calibrate (error message during calibration) | |
| Jumpy, erratic, or questionable readings | |
| Slow response time | |
| Failed calibration check | |
| Potential pH problem | Solution |
| Lack of electrolyte or expired electrolyte | Refill electrolyte (refillable probes only) or replace probe (non-refillable) |
| Clogged reference junction | Clean or replace reference junction |
| Dirty glass bulb | Clean bulb |
| Scratched glass bulb | Replace probe |
| pH probe stored dry or in DI water | Soak pH probe in pH 4 buffer or electrolyte solution. Soaking for several hours or overnight is typically needed. |
| Contaminated standard | Use fresh standard. Rinse probes thoroughly between uses and with a small amount fresh standard before submersing. |

4.5 CONDUCTIVITY (SPECIFIC CONDUCTIVITY AT 25 °C)

Conductivity is to be measured and reported as specific conductivity at 25 °C. The specific conductivity calibration, calibration verification, and maintenance guidelines included in this section are to be used as a supplement to the meter manufacturer guidelines and DWQ Wastewater/Groundwater Certification Branch Rules and Policy and not as a replacement.

4.5.1 Conductivity Temperature Dependence

Accurate conductivity measurements depend on accurate temperature measurements and accurate temperature compensation. It is critical that the temperature sensor used for temperature compensation be working properly and be submerged along with the conductivity probe when calibrating and making measurements. Calibrating under controlled conditions close to 25 °C will help reduce any temperature compensation errors during calibration.

Annual Automatic Temperature Compensation Verification for Conductivity

DWQ Certification Branch policy requires that the internal Automatic Temperature Compensator (ATC) be verified every 12 months and the process documented. The DWQ Certification Branch outlines the procedure to verify the ATC in the [Guidelines for the Field Analysis of Conductivity](#) document on their website.

4.5.2 Conductivity Calibration Standards

Conductivity standards are available as potassium chloride (KCl) standards, sodium chloride (NaCl) standards, or “442™” standards. Follow the manufacturer’s instructions regarding the type of conductivity standards to use. Generally, use the standard which best corresponds to the temperature-compensation factor programmed into meter. The values of the conductivity standards used to calibrate and check the meter should bracket the expected environmental sample range.

4.5.3 Conductivity Calibration

Good practices for calibration are outlined below. These are intended to supplement the manufacturer’s guidelines and are not meant to be used as a replacement.

- Ensure the conductivity probe is clean and free of dirt, residue, and debris.
NOTE: *The conductivity cell should read zero in air. If it does not, clean the cell following the manufacturer’s instructions.*
- Prior to calibration or a calibration check, rinse the conductivity probe with a small amount of the calibration standard and discard rinse.

- When immersing the conductivity probe in the calibration standard, make sure the conductivity cell and temperature sensor are fully submerged and that no air bubbles are in the conductivity cell.
- Make sure “specific conductivity” at 25 °C is selected in the calibration menu.
- Allow the conductivity and temperature readings to stabilize (typically one minute) before calibrating.
- Record both the pre-calibration and post-calibration values on the calibration sheet.
- After calibration is completed, verify the conductivity calibration in at least one other standard. Bracket the range of anticipated measurements. The conductivity reading must be within 10% of the calibration standard.
NOTE: *Under DWQ certification policy for regular laboratory certification, a one-point calibration at a high standard followed by a check in a mid-range and low-range standard is required. For field parameter certification, one check is required after calibration and it is recommended that it be at a lower range.*
- When performing calibration checks, it is recommended to document the acceptance range for each standard on the calibration/calibration verification sheet to make it easier for the analyst to know when the meter exceeds the acceptance range (i.e. a standard of 1000 µS/cm would have an acceptance range of 900-1100 µS/cm). This is done on the DWQ AMS standard calibration/calibration verification sheet (Appendix C).

4.5.4 Conductivity Calibration Verification and Data Validation

In order to validate the conductivity readings, calibration verifications must be performed at the end of a sampling run. Mid-day calibration verifications are also recommended. The calibration verification involves following all the same steps in the calibration routine without recalibrating the meter. When the conductivity probe is under stable calibration conditions, record the following readings:

- Time
- Conductivity Standard Value
- Probe Reading Value

In order to fully validate all results, the calibration check standards must bracket the range of field measurements. If the meter does not read within $\pm 10\%$ of the conductivity standards, the meter must be recalibrated. However, do not recalibrate until all standards are checked.

In the event of a failed calibration verification (meter reads outside of $\pm 10\%$ of standard value), flag the data between the initial calibration and the failed calibration verification with a remark code of J12 and document the extent of calibration drift in the comments

section monthly data submittal sheets, as described in Section 4.1.4. Calibration Verification and Data Validation and as demonstrated in Appendix A.

4.5.5 Maintenance and Troubleshooting

Follow the manufacturer’s guidelines for maintenance and troubleshooting. Table 4 summarizes the most common conductivity problems and solutions. Appendix G provides more detailed troubleshooting and maintenance tips.

Table 4: Conductivity Troubleshooting

| Symptoms | |
|---|---|
| Unable to calibrate (error message during calibration) | |
| Questionable readings | |
| Conductivity unstable or inaccurate | |
| Failed conductivity check | |
| Potential problem | Solution |
| Dirty conductivity cell | Clean cell per manufacturer’s instructions Confirm probe reads close to zero in dry air |
| Contaminated standards | Clean cell per manufacturer’s instructions Use fresh, certified standards Never reuse standards Low level-standards are easily contaminated; use with extra caution Check expiration date of standard Rinse probes thoroughly between uses and with a small amount fresh standard before submersing in the standard. |
| Improper calibration technique <ul style="list-style-type: none"> • cell not fully submerged • bubbles in conductivity cell | Follow manufacturer’s instructions carefully |
| Temperature-compensation error | Ensure automatic temperature compensation (ATC) factor programmed in meter matches calibration solution Follow ATC check for conductivity in DWQ Wastewater/Groundwater Laboratory Certification Guidelines Return meter to manufacturer for repair if it fails ATC check |

5 SAMPLE COLLECTION AND PRESERVATION

5.1 GENERAL

Section 5 contains parameter-specific guidelines for collecting water samples for laboratory analysis. All laboratory analysis must be performed at a DWQ certified laboratory. The proper collection technique for each parameter may vary depending on the analytical method. Laboratory methods not prescribed by 40 CFR 136 may be used if granted alternative test procedure approval by EPA Region IV. The application for an alternate test procedure process is outlined in 40 CFR 136.4 and 40 CFR 136.5. Application for alternate test procedures should be discussed with DWQ.

5.1.1 Bottles and Preservation

Appropriate bottles and preservation techniques must be used. Consult EPA 40 CFR Part 136, Table II ([March 12, 2007: Vol. 72, No. 47](#) and [March 26, 2007: Vol. 72., No. 57](#)) for the appropriate bottles and containers. Collection and preservation guidelines used by DWQ staff can be found on the DWQ Laboratory Branch website at the [Collection and Preservation of Water Quality Samples](#) webpage.

Preservation on ice

Samples requiring ice preservation must be iced within 15 minutes of sampling. Personnel should ensure that the ice does not submerge the sample containers, thereby preventing cross-contamination. Steps to prevent submersion of the sample containers include:

- Placing bottles upright in cooler in ice with lids above the iceline and frequently draining melted icewater so as to ensure only solid ice is in cooler
- Placing bottles in sealed plastic bags before inserting into ice

NOTE: *Ice or ice slurry must be used for keeping samples cool. Use of frozen ice packs is not an acceptable alternative.*

5.1.2 Sample Documentation

Basic information required to verify sample preservation and holding time requirements include:

- Sample identification including the number and type of containers and sampling location;
- Sample collector (printed name or signature where required);
- Date and time of sample collection;
- The parameter and/or analytical method to be performed;
- Sample type (grab, composite);
- Preservation status; temperature and chemical preservatives

These requirements are documented in the DWQ Wastewater and Groundwater Certification Memorandum from 6/20/2007 entitled: [Required Documentation for Sample Preservation and Hold Time](#).

5.2 CHLOROPHYLL A

Samples are collected as either grab samples or photic zone samples depending on site characteristics. When water depth allows, samples are typically collected as vertically integrated depth samples in the photic zone as described in Section 3.2.4. Photic Zone Sampling. To collect a photic zone sample, water must be deep enough to allow a Secchi depth measurement and to allow the use of the vertically integrated sampler (i.e. Labline®) to collect water at twice the Secchi depth.

When water depth is not sufficient for photic zone sampling, collect chlorophyll *a* samples as grab samples as described in Section 3.2.3. Grab Samples.

Regardless of the sampling method, all chlorophyll *a* samples must be collected into a bottle that will protect the sample from light. Brown opaque bottles (plastic or glass) are commonly used and strongly recommended. Sampling volume depends on the analytical method. The DWQ lab utilizes EPA Method 445.0, Revision 1.2, September 1997 and the collection method is:

- Minimum of 500 mL in plastic amber bottle
- Cool to 6°C
- Maximum hold time of 24 hours prior to filtering. After filtering, samples can be frozen at -20°C for 3 ½ weeks.

5.3 CONDUCTIVITY (SPECIFIC CONDUCTIVITY AT 25 °C)

Conductivity is normally measured in the field using a field meter, but may also be collected as a grab sample for laboratory analysis. If collecting for laboratory analysis, sample requirements include:

- Cool to 6°C
- Maximum hold time of 28 days

5.4 FECAL COLIFORM

Guidelines for collecting fecal samples include:

- 1.) Collect sample directly into sterilized plastic or glass bottles containing sodium thiosulfate and EDTA reagents. Follow grab collection sample method (Section 3.2.3).
- 2.) Do not rinse bottle with sample.
- 3.) Fill sample bottle to within 1-2 inches from the top to allow mixing of sample before analysis.
- 4.) Use caution to avoid contaminating the sample with fingers, gloves, or other materials.
- 5.) Cool to 6°C and return to lab within 6 hours from time of collection.

5.5 NUTRIENTS

Nutrient samples collected by the coalitions include:

- Ammonia (NH₃)
- Total Kjeldahl Nitrogen (TKN)
- Nitrate plus Nitrite (NO₃ + NO₂)
- Total Phosphorus (TP)

Nutrients are collected as grab samples at most sites. However, at sites where chlorophyll a is collected as a photic zone sample, nutrients are also to be collected as a photic zone sample. At sites where chlorophyll a samples are taken only seasonally as photic zone samples but nutrient samples are taken year round, nutrient samples are to be taken year round as photic zone samples.

Multiple methods are approved for nutrient analysis. Follow the method guidelines regarding sample preservation. Generally, NH₃, TKN, NO₃ + NO₂, and TP can all be collected in one bottle and are preserved with sulfuric acid to a pH less than 2. Acid may be added to the bottle before sample collection or after collection in the field. Follow all appropriate safety measures when handling concentrated acids. General requirements when collecting nutrients include:

- Add H₂SO₄ to pH<2 (to 500 ml sample add 2.0 ml 25% H₂SO₄, check pH and add more acid if necessary)
- Cool to 6°C
- Maximum holding time is 28 days

5.6 TOTAL RECOVERABLE METALS

Historically, the following total recoverable metals have been sampled under the coalition program:

- Aluminum (Al)
- Arsenic (As)
- Cadmium (Cd)
- Chromium (Cr)
- Copper (Cu)
- Iron (Fe)
- Lead (Pb)
- Manganese (Mn)
- Mercury (Hg)
- Nickel (Ni)
- Zinc (Zn)

On April 3, 2007, DWQ temporarily suspended the collection and analysis of total recoverable metals as required by the NPDES Discharge Monitoring Coalitions through the Memorandums of Agreement as the division reviewed its metals monitoring and standards. This suspension is being continued by DWQ. A copy of the memo is presented in Appendix H. Coalitions retain the option to continue total recoverable metals monitoring during the suspension.

Multiple methods are approved for metals analyses. Check with the method specific requirements for sample collection and preservation. For most methods, all metal parameters may be collected in one bottle. If utilizing EPA Method 1631 for Hg analysis, Hg must be collected separately following EPA Method 1669 for clean sample collection.

Samples for the coalition program have historically been collected either as standard grab samples or grab samples utilizing clean sampling techniques based on EPA Method 1669.

Total recoverable metals (except Hg) collection requirements include:

- HNO₃ to pH <2
NOTE: *Per 40 CFR 136, Table II, Footnote 19, an aqueous sample may be collected and shipped without acid preservation; however, acid must be added at least 24 hours before analysis.*
- Holding time of six months

Hg analysis using EPA Method 245.1

- HNO₃ to pH <2
NOTE: *Per EPA Method 245.1, the sample may be acidified at the time of collection or preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, held for 16 hours, and then verified to pH <2 just prior to withdrawing an aliquot for processing.*
- Holding time of 28 days

Trace level Hg analysis using EPA Method 1631:

Per 40 CFR 136, Table II, Footnote 17, samples collected for the determination of trace level mercury (<100 ng/L) using EPA Method 1631 must be collected in a tightly capped fluoropolymer or glass bottle and preserved with BrCl or HCl solution within 48 hours of sample collection. The time to preservation may be extended to 28 days if a sample is oxidized in the sample bottle. The sample has a 90 day holding time.

Clean sampling techniques for metals

EPA Method 1669 was designed to preclude contamination during the collection, transport, and analysis of samples. Additionally, it was designed to provide the procedures necessary to produce reliable results at the lowest possible water quality criteria published by the EPA. The method is performance-based, meaning that alternative procedures may be used, so long as those procedures are demonstrated to yield reliable results. Any coalition contract lab utilizing this method will have an SOP

outlining their modifications to the technique. This sampling method must be employed when using EPA Method 1631 for Hg analysis. It may also be used to collect other metals samples.

5.7 SUSPENDED RESIDUE

Suspended residue is often referred to as total suspended solids (TSS). Suspended residue is collected as a grab sample in the coalition program. Requirements for collecting suspended residue samples include:

- Cool to 6°C
- Maximum hold time of 7 days

5.8 LAB TURBIDITY

Lab turbidity (also referred to as “turbidity”) is collected as a grab sample in the coalition program. Requirements for collecting turbidity samples include:

- Cool to 6°C
- Maximum holding time is 48 hours. However, samples should be submitted to the lab as soon as possible.

6 STANDARD CLEANING PROCEDURES

All sampling equipment must be properly cleaned before sampling. Check with each analytical method for any parameter-specific equipment cleaning instructions. General recommendations include:

6.1 GENERAL SAMPLING EQUIPMENT

Sampling equipment should be washed with phosphate-free laboratory detergent and rinsed with hot tap water before long-term storage.

6.2 LABLINE® SAMPLERS

For Lablines®, clean with phosphate-free detergent and rinse at least three times with distilled deionized water. A common practice is to cover the top of the Labline® with foil in order to prevent contamination and to show that the Labline® has been cleaned. Between sites, rinse with distilled water. At each site, rinse the Labline® with surface water prior to taking the sample.

6.3 FIELD METERS

Follow manufacturers' instructions for cleaning. Keep meter body free of dirt by wiping with a damp cloth. Rinse probes between uses and before storage. Keep probes free of dirt and debris. Store probes per manufacturers' instructions.

6.4 COOLERS AND SHIPPING CONTAINERS

All ice chests and reusable shipping containers should be washed as needed with a mild, phosphate free detergent (interior and exterior), rinsed with tap water, and air dried before storage.

6.5 SAMPLING CONTAINERS

Containers that are purchased as pre-cleaned should be certified by the manufacturer or checked to ensure that the parameters tested are below the published reporting limits. Manufacturer certificates for glass bottles should be kept on file. Containers should be stored in a manner that does not leave them susceptible to contamination by dust or other particulates and should remain capped until use. Any containers showing evidence of contamination should be discarded.

It is a good laboratory practice to periodically check bottles for contamination attributed to storage conditions at the lab by filling representative containers with analyte-free water, adding the appropriate preservatives, and submitting them to the lab for analysis. Any container lots showing analyte levels at or above reporting limits should be discarded.

7 DWQ FIELD VISITS AND QA/QC STUDIES

7.1 FIELD VISITS

At least one time per year, DWQ staff will observe field sampling and summarize the field visit in a letter that will be sent to the coalition chairman. Field visits will involve following a monitor through a day of sampling, from the initial calibration until the end-of-the-day transfer of samples to the laboratory. Visits will include reviewing:

- station location
- meter maintenance
- calibration
- quality assurance/quality control practices
- sampling technique
- sample preservation, handling, and transport
- safety practices
- documentation procedures

Appendix I includes an example of a field visit checklist.

7.2 QA/QC STUDIES

The coalition program may occasionally conduct special QA/QC study to assess consistency of results among coalition contract labs and the DWQ. These special studies may include:

- Field parameter measurement comparison using two or more field meters;
- Split sampling study in which split samples for a certain parameter are taken and analyzed by the DWQ lab and the coalition contract lab(s). Multiple labs may be involved in the split sampling study.

8 REFERENCES AND HYPERLINKS

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North Carolina Division of Water Quality

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Guidelines for the Field Analysis of pH

http://h2o.enr.state.nc.us/lab/documents/GUIDELINESFORFIELDANALYSISOFpH69_07final.pdf

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Guidelines for the Field Analysis of Conductivity
<http://h2o.enr.state.nc.us/lab/documents/GUIDELINESFORFIELDANALYSISISOFSPECIFICCONDUCTIVITY9-07final.pdf>
(last accessed 2/01/08)

Data qualifying codes
<http://h2o.enr.state.nc.us/lab/qa/qualifier.htm>
(last accessed 2/01/08)

DWQ Laboratory Section Quality Assurance website
<http://h2o.enr.state.nc.us/lab/qa.htm>
(last accessed 2/20/08)

Collection and preservation of water quality samples
<http://h2o.enr.state.nc.us/lab/qa/collpreswq.htm>
(last accessed 1/25/08)

Required Documentation for Sample Preservation and Hold Time
http://h2o.enr.state.nc.us/lab/documents/Preservationmemo6_07.pdf
(last accessed 1/25/07)

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APPENDIX A. FLAGGING DATA TAKEN PRIOR TO FAILED CALIBRATION VERIFICATIONS

For data taken between the initial calibration and a failed calibration verification, flag data by using a “J12” in the remark code column and document the extent of calibration drift in the comments column.

J12 indicates that “the calibration verification did not meet the calibration acceptance criteria for field parameters.”

The full list [DWQ data remark codes](#) is documented in the MOAs and available on the [DWQ Laboratory Section Quality Assurance website](#) .

| Station | Date (m/d/yyyy) | Time (hh:mm) | Depth (m) | Temp (°C) | Temp_rmk | DO (mg/l) | DO_rmk | pH (su) | pH_rmk | Conductivity (µmhos/cm) | Conductivity_rmk | Comments |
|----------|-----------------|--------------|-----------|-----------|----------|-----------|--------|---------|--------|-------------------------|------------------|--|
| A1234567 | 8/19/2007 | 15:30 | 0.1 | 25.2 | | 7.8 | | 6.9 | | 133 | | |
| A9876543 | 8/20/2007 | 11:50 | 0.1 | 27.2 | | 7.1 | | 7.2 | J12 | 125 | | Calibration drift - 0.3 SU from 7.0 SU |
| A8765432 | 8/20/2007 | 13:05 | 0.1 | 28.0 | | 6.5 | | 6.3 | J12 | 122 | | Calibration drift - 0.3 SU from 7.0 SU |
| A7654321 | 8/20/2007 | 13:30 | 0.1 | 25.0 | | 6.7 | | 6.9 | | 119 | | |
| A6543210 | 8/20/2007 | 14:50 | 0.1 | 17.0 | | 5.5 | | 6.7 | | 120 | | |
| A1357924 | 8/21/2007 | 16:10 | 0.1 | 22.1 | | 3.1 | | 6.2 | | 233 | J12 | Calibration drift +15% from 100 uS/cm |
| A0246813 | 8/24/2007 | 9:30 | 0.1 | 19.7 | | 8.3 | J12 | 7.0 | | 99 | | Calibration drift - 0.9 mg/L from 8.6 mg/L |
| A0246813 | 8/24/2007 | 11:30 | 0.1 | 12.0 | | 8.9 | J12 | 7.3 | | 115 | | Calibration drift - 0.9 mg/L from 8.6 mg/L |

See
NOTE

NOTE: Columns on data submittal sheet between Conductivity_rmk column and Comments column not shown

APPENDIX B. DATA REMARK CODES

When reporting data, the DWQ's data remark codes must be used to provide additional information regarding data quality and interpretation. The current set (codes are subject to change) of remark codes to be used is provided below. Use the following website to check for changes in the remark codes under the link "Data Remark Codes used by DWQ programs": <http://h2o.enr.state.nc.us/lab/qa.htm>.

Data Remark Codes For Use with Coalition Data as of 5/05/2008

| Data Remark Code | Code Definition |
|------------------|--|
| A | <p>Value reported is the mean (average) of two or more determinations. This code is to be used if the results of two or more discrete and separate samples are averaged. These samples shall have been processed and analyzed independently (e.g. field duplicates, different dilutions of the same sample). This code is not required for BOD or coliform reporting since averaging multiple dilutions for these parameters is fundamental to those methods.</p> |
| B | <p>Results are based upon colony counts outside the acceptable range and should be used with caution. This code applies to microbiological tests and specifically to membrane filter (MF) colony counts. It is to be used if less than 100% sample was analyzed and the colony count is generated from a plate in which the number of coliform colonies exceeds the ideal ranges indicated by the method. These ideal ranges are defined in the method as:</p> <p><i>Fecal coliform bacteria: 20-60 colonies Total coliform bacteria: 20-80 colonies</i></p> <ul style="list-style-type: none"> B1. Countable membranes with less than 20 colonies. Reported value is estimated or is a total of the counts on all filters reported per 100 mL. B2. Counts from all filters were zero. The value reported is based on the number of colonies per 100 mL that would have been reported if there had been one colony on the filter representing the largest filtration volume (reported as a less than "<" value). B3. Countable membranes with more than 60 or 80 colonies. The value reported is calculated using the count from the smallest volume filtered and reported as a greater than ">" value. B4. Filters have counts of both >60 or 80 and <20. Reported value is a total of the counts from all countable filters reported per 100 mL. B5. Too many colonies were present; too numerous to count (TNTC). TNTC is generally defined as > 150 colonies. The numeric value represents the maximum number of counts typically accepted on a filter membrane (60 for fecal and 80 for total), multiplied by 100 and then divided by the smallest filtration volume analyzed. This number is reported as a greater than value. B6. Estimated Value. Blank contamination evident. B7. Many non-coliform colonies or interfering non-coliform growths are present. In this competitive situation, the reported coliform value may under-represent actual coliform density. |
| C | <p>Total residual chlorine was present in sample upon receipt in the laboratory; value is estimated. Generally applies to cyanide, phenol, NH₃, TKN, coliform, and organics)</p> |

APPENDIX B (CONT'D). DATA REMARK CODES.

| Data Qualifier Code | Code Definition |
|---------------------|--|
| G | <p>A <u>single</u> quality control failure occurred during biochemical oxygen demand (BOD) analysis. The sample results should be used with caution.</p> <ul style="list-style-type: none"> G1. The dissolved oxygen (DO) depletion of the dilution water blank exceeded 0.2 mg/L. G2. The bacterial seed controls did not meet the requirement of a DO depletion of at least 2.0 mg/L and/or a DO residual of at least 1.0 mg/L. G3. No sample dilution met the requirement of a DO depletion of at least 2.0 mg/L and/or a DO residual of at least 1.0 mg/L. G4. Evidence of toxicity was present. This is generally characterized by a significant increase in the BOD value as the sample concentration decreases. The reported value is calculated from the highest dilution representing the maximum loading potential and should be considered an estimated value. G5. The glucose/glutamic acid standard exceeded the range of 198± 30.5 mg/L. G6. The calculated seed correction exceeded the range of 0.6 to 1.0 mg/L. G7. Less than 1 mg/L DO remained for all dilutions set. The reported value is an estimated greater than value and is calculated for the dilution using the least amount of sample. G8. Oxygen usage is less than 2 mg/L for all dilutions set. The reported value is an estimated less than value and is calculated for the dilution using the most amount of sample. G9. The DO depletion of the dilution water blank produced a negative value. |
| J | <p>Estimated value; value may not be accurate. This code is to be used in the following instances:</p> <ul style="list-style-type: none"> J1. Surrogate recovery limits have been exceeded; J2. The reported value failed to meet the established quality control criteria for either precision or accuracy; J3. The sample matrix interfered with the ability to make any accurate determination; J4. The data is questionable because of improper laboratory or field protocols (e.g. composite sample was collected instead of grab, plastic instead of glass container) J5. Temperature limits exceeded (samples frozen or >6° C) during transport or not verifiable (e.g., no temperature blank provided); non-reportable for NPDES compliance monitoring. J6. The laboratory analysis was from an unpreserved or improperly chemically preserved sample. The data may not be accurate. J7. This qualifier is used to identify analyte concentration exceeding the upper calibration range of the analytical instrument/method. The reported value should be considered estimated. J8. Temperature limits exceeded (samples frozen or >6°C during storage. The data may not be accurate. J9. The reported value is determined by a one-point estimation rather than against a regression equation. The estimated concentration is less than the laboratory practical quantitation limit and greater than the laboratory method detection limit. J10. Unidentified peak; estimated value. J11. The reported value is determined by a one-point estimation rather than against a regression equation. The estimated concentration is less than the laboratory practical quantitation limit and greater than the laboratory method detection limit. <i>This code is used when an MDL has not been established for the analyte in question.</i> J12. The calibration verification did not meet the calibration acceptance criterion for field parameters <p><u>Note:</u> A "J" value shall not be used if another code applies (ex. N, V, M).</p> |

APPENDIX B (CONT'D). DATA REMARK CODES

| Data Qualifier Code | Code Definition |
|---------------------|---|
| M | Sample and duplicate results are "out of control." The sample is non-homogenous (e.g. VOA soil). The reported value is the <u>lower</u> value of duplicate analyses of a sample. |
| N | <p>Presumptive evidence of presence of material; estimated value. This code is to be used if:</p> <p>N1. The component has been tentatively identified based on mass spectral library search;</p> <p>N2. There is an indication that the analyte is present, but quality control requirements for confirmation were not met (i.e., presence of analyte was not confirmed by alternate procedures).</p> <p>N3. This code shall be used if the level is too low to permit accurate quantification, but the estimated concentration is less than the laboratory practical quantitation limit and greater than the laboratory method detection limit. <i>This code is not routinely used for most analyses.</i></p> <p>N4. This code shall be used if the level is too low to permit accurate quantification, but the estimated concentration is less than the laboratory practical quantitation limit and greater than the instrument noise level. <i>This code is used when an MDL has not been established for the analyte in question.</i></p> <p>N5. The component has been tentatively identified based on a retention time standard.</p> |
| P | Elevated practical quantitation limit (PQL)* due to matrix interference and/or sample dilution. |
| Q | <p>Holding time exceeded. These codes shall be used if the value is derived from a sample that was received, prepared and/or analyzed after the approved holding time restrictions for sample preparation and analysis. The value does not meet NPDES requirements.</p> <p>Q1. Holding time exceeded prior to receipt by lab</p> <p>Q2. Holding time exceeded following receipt by lab</p> |
| S | Not enough sample provided to prepare and/or analyze a method-required matrix spike (MS) and/or duplicate (MSD). |
| U | Indicates that the analyte was analyzed for but not detected above the reported practical quantitation limit (PQL)*. The number value reported with the "U" qualifier is equal to the laboratory's PQL*. |
| V | <p>Indicates the analyte was detected in both the sample and the associated method blank.</p> <p><u>Note:</u> The value in the blank shall not be subtracted from the associated samples.</p> |
| X | <p>Sample not analyzed for this constituent. This code is to be used if:</p> <p>X1. Sample not screened for this compound.</p> <p>X2. Sampled, but analysis lost or not performed-field error</p> <p>X3. Sampled, but analysis lost or not performed-lab error</p> |
| Y | Elevated PQL* due to insufficient sample size |
| Z | <p>The presence or absence of the analyte cannot be verified. The sample analysis/results are not reported due to:</p> <p>Z1. Inability to analyze the sample.</p> <p>Z2. Questions concerning data reliability.</p> |

* The Practical Quantitation Limit (PQL) is defined as the lowest level achievable among laboratories within specified limits during routine laboratory operation. The Practical Quantitation Limit (PQL) is "about three to five times the method detection limit (MDL) and represents a practical and routinely achievable detection level with a relatively good certainty that any reported value is reliable." (APHA, AWWA, WEF. 1992. Standard Methods for the Examination of Water and Wastewater, 18th ed.)

APPENDIX C. DWQ AMS FIELD CALIBRATION SHEET

Water Quality Monitoring Field Meter Calibration Sheet

Collector(s): _____

Study: _____

Sampling Location: _____

Meter Model: _____

Meter / Sonde Serial No: _____

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

Miscellaneous (Does not apply to YSI 85 or Accumet Meters)

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

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

Dissolved Oxygen (mg/L)

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

Specific Conductance (µS/cm at 25°C)

| | Dry Air ^{1,2} Zero (0) | | Conductivity Standard ³ Value: | | Calibration Check Value: | | ±10% Ranges for Sp. Cond. Standard Range 10090 to 110 447 402 to 492 1,000900 to 1,100 10,0009,000 to 11,000 15,000 13,500 to 16,500 58,670 52,803 to 64,537 |
|--------------------------|------------------------------------|---------------------------------------|--|---------------------------------------|-----------------------------|--|---|
| | Initial Meter Reading | Calibrated ⁴ Meter Reading | Initial Meter Reading | Calibrated ⁴ Meter Reading | Initial Meter Reading | | |
| Pre-Sampling Calibration | | | | | | | |
| Post-Sampling Check | Within ± 2? Y / N | | Within ±10%? Y / N | | Within ±10% Y / N | | |

NOTE: Quanta reads in mS/cm; move decimal 3 places right for µS/cm.

¹ Dry Air CALIBRATIONS are conducted for 4a and MS5 Hydrolabs only.

² Dry Air CHECKS (confirmation of zero in dry air) are conducted for YSI 85, YSI 6920, & Quanta meters.

³ Conductivity standards are used to CHECK the YSI 85 meter and to CALIBRATE all Hydrolab meters and the YSI 6920.

⁴ Does not apply to Dry Air CHECKS or Conductivity Standard CHECKS (leave blank).

pH (SU)

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

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

Comments: _____

2/19/2008

APPENDIX D. DWQ AMS DISSOLVED OXYGEN SOLUBILITY TABLE AND DISSOLVED OXYGEN CORRECTION CHART

To verify dissolved oxygen reading:

- Set up probe under stable calibration conditions. When stable, record temperature reading.
- Look up temperature on chart. The corresponding DO value, given in mg/L, is the theoretical amount of oxygen that would be dissolved in water at sea level (barometric pressure = 760 mm Hg and altitude = 0 ft).
- To adjust for barometric pressure or altitude, multiply the theoretical DO value from the table by the altitude or barometric pressure correction value given in the DO correction chart on the following page.

Sea Level (*Uncorrected D.O. Values*) Dissolved Oxygen (D.O.) TABLE

Altitude at Sea Level = 0 feet

Barometric Pressure (BP) at Sea Level = 760 mm Hg

| Temp (°C) | 0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | Temp (°C) |
|-----------|------|------|------|------|------|------|------|------|------|------|-----------|
| 0 | 14.6 | 14.6 | 14.5 | 14.5 | 14.5 | 14.4 | 14.4 | 14.3 | 14.3 | 14.3 | 0 |
| 1 | 14.2 | 14.2 | 14.1 | 14.1 | 14.1 | 14.0 | 14.0 | 13.9 | 13.9 | 13.9 | 1 |
| 2 | 13.8 | 13.8 | 13.8 | 13.7 | 13.7 | 13.6 | 13.6 | 13.6 | 13.5 | 13.5 | 2 |
| 3 | 13.5 | 13.4 | 13.4 | 13.4 | 13.3 | 13.3 | 13.2 | 13.2 | 13.2 | 13.1 | 3 |
| 4 | 13.1 | 13.1 | 13.0 | 13.0 | 13.0 | 12.9 | 12.9 | 12.9 | 12.8 | 12.8 | 4 |
| 5 | 12.8 | 12.7 | 12.7 | 12.7 | 12.6 | 12.6 | 12.6 | 12.5 | 12.5 | 12.5 | 5 |
| 6 | 12.4 | 12.4 | 12.4 | 12.4 | 12.3 | 12.3 | 12.3 | 12.2 | 12.2 | 12.2 | 6 |
| 7 | 12.1 | 12.1 | 12.1 | 12.0 | 12.0 | 12.0 | 12.0 | 11.9 | 11.9 | 11.9 | 7 |
| 8 | 11.8 | 11.8 | 11.8 | 11.8 | 11.7 | 11.7 | 11.7 | 11.6 | 11.6 | 11.6 | 8 |
| 9 | 11.6 | 11.5 | 11.5 | 11.5 | 11.4 | 11.4 | 11.4 | 11.4 | 11.3 | 11.3 | 9 |
| 10 | 11.3 | 11.3 | 11.2 | 11.2 | 11.2 | 11.2 | 11.1 | 11.1 | 11.1 | 11.1 | 10 |
| 11 | 11.0 | 11.0 | 11.0 | 11.0 | 10.9 | 10.9 | 10.9 | 10.9 | 10.8 | 10.8 | 11 |
| 12 | 10.8 | 10.8 | 10.7 | 10.7 | 10.7 | 10.7 | 10.6 | 10.6 | 10.6 | 10.6 | 12 |
| 13 | 10.5 | 10.5 | 10.5 | 10.5 | 10.4 | 10.4 | 10.4 | 10.4 | 10.4 | 10.3 | 13 |
| 14 | 10.3 | 10.3 | 10.3 | 10.2 | 10.2 | 10.2 | 10.2 | 10.1 | 10.1 | 10.1 | 14 |
| 15 | 10.1 | 10.1 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 9.9 | 9.9 | 9.9 | 15 |
| 16 | 9.9 | 9.8 | 9.8 | 9.8 | 9.8 | 9.8 | 9.7 | 9.7 | 9.7 | 9.7 | 16 |
| 17 | 9.7 | 9.6 | 9.6 | 9.6 | 9.6 | 9.6 | 9.5 | 9.5 | 9.5 | 9.5 | 17 |
| 18 | 9.5 | 9.4 | 9.4 | 9.4 | 9.4 | 9.4 | 9.4 | 9.3 | 9.3 | 9.3 | 18 |
| 19 | 9.3 | 9.3 | 9.2 | 9.2 | 9.2 | 9.2 | 9.2 | 9.1 | 9.1 | 9.1 | 19 |
| 20 | 9.1 | 9.1 | 9.1 | 9.0 | 9.0 | 9.0 | 9.0 | 8.97 | 8.9 | 8.9 | 20 |
| 21 | 8.9 | 8.9 | 8.9 | 8.9 | 8.8 | 8.8 | 8.8 | 8.8 | 8.8 | 8.8 | 21 |
| 22 | 8.7 | 8.7 | 8.7 | 8.7 | 8.7 | 8.7 | 8.6 | 8.6 | 8.6 | 8.6 | 22 |
| 23 | 8.6 | 8.6 | 8.5 | 8.5 | 8.5 | 8.5 | 8.5 | 8.5 | 8.4 | 8.4 | 23 |
| 24 | 8.4 | 8.4 | 8.4 | 8.4 | 8.4 | 8.3 | 8.3 | 8.3 | 8.3 | 8.3 | 24 |
| 25 | 8.3 | 8.2 | 8.2 | 8.2 | 8.2 | 8.2 | 8.2 | 8.2 | 8.1 | 8.1 | 25 |
| 26 | 8.1 | 8.1 | 8.1 | 8.1 | 8.1 | 8.0 | 8.0 | 8.0 | 8.0 | 8.0 | 26 |
| 27 | 8.0 | 8.0 | 7.9 | 7.9 | 7.9 | 7.9 | 7.9 | 7.9 | 7.9 | 7.8 | 27 |
| 28 | 7.8 | 7.8 | 7.8 | 7.8 | 7.8 | 7.8 | 7.7 | 7.7 | 7.7 | 7.7 | 28 |
| 29 | 7.7 | 7.7 | 7.7 | 7.7 | 7.6 | 7.6 | 7.6 | 7.6 | 7.6 | 7.6 | 29 |
| 30 | 7.6 | 7.5 | 7.5 | 7.5 | 7.5 | 7.5 | 7.5 | 7.5 | 7.5 | 7.4 | 30 |
| 31 | 7.4 | 7.4 | 7.4 | 7.4 | 7.4 | 7.4 | 7.4 | 7.3 | 7.3 | 7.3 | 31 |
| 32 | 7.3 | 7.3 | 7.3 | 7.3 | 7.3 | 7.2 | 7.2 | 7.2 | 7.2 | 7.2 | 32 |
| 33 | 7.2 | 7.2 | 7.2 | 7.1 | 7.1 | 7.1 | 7.1 | 7.1 | 7.1 | 7.1 | 33 |
| 34 | 7.1 | 7.1 | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 34 |
| 35 | 6.9 | 6.9 | 6.9 | 6.9 | 6.9 | 6.9 | 6.9 | 6.9 | 6.9 | 6.8 | 35 |

* All D.O. values are in mg/L

Correction Factor at Sea Level = 1.0

APPENDIX D (CONT'D). DWQ AMS DISSOLVED OXYGEN SOLUBILITY TABLE AND DISSOLVED OXYGEN CORRECTION CHART

| Altitude (ft) | Barometric Pressure (mmHg) | Correction Factor | Altitude (ft) | Barometric Pressure (mmHg) | Correction Factor |
|---------------|----------------------------|-------------------|---------------|----------------------------|-------------------|
| -300 | 768 | 1.012 | 2200 | 699 | 0.920 |
| -200 | 765 | 1.008 | 2300 | 697 | 0.917 |
| -100 | 762 | 1.004 | 2400 | 695 | 0.914 |
| 0 | 760 | 1 | 2500 | 692 | 0.910 |
| 100 | 757 | 0.996 | 2600 | 689 | 0.907 |
| 200 | 755 | 0.993 | 2700 | 686 | 0.903 |
| 300 | 752 | 0.989 | 2800 | 684 | 0.900 |
| 400 | 749 | 0.985 | 2900 | 682 | 0.897 |
| 500 | 746 | 0.981 | 3000 | 679 | 0.893 |
| 600 | 743 | 0.978 | 3100 | 676 | 0.890 |
| 700 | 740 | 0.974 | 3200 | 673 | 0.886 |
| 800 | 737 | 0.970 | 3300 | 671 | 0.883 |
| 900 | 735 | 0.967 | 3400 | 669 | 0.880 |
| 1000 | 732 | 0.963 | 3500 | 666 | 0.876 |
| 1100 | 729 | 0.959 | 3600 | 663 | 0.873 |
| 1200 | 727 | 0.956 | 3700 | 661 | 0.870 |
| 1300 | 724 | 0.952 | 3800 | 658 | 0.866 |
| 1400 | 721 | 0.949 | 3900 | 656 | 0.863 |
| 1500 | 718 | 0.945 | 4000 | 654 | 0.860 |
| 1600 | 715 | 0.941 | 4100 | 651 | 0.857 |
| 1700 | 713 | 0.938 | 4200 | 648 | 0.853 |
| 1800 | 710 | 0.934 | 4300 | 646 | 0.850 |
| 1900 | 708 | 0.931 | 4400 | 644 | 0.847 |
| 2000 | 705 | 0.927 | 4500 | 641 | 0.844 |
| 2100 | 702 | 0.924 | | | |

How to Correct D.O. Table Values

Corrected D.O. value = value from Sea Level D.O. Table * Correction Value

1. Use the temperature displayed on your meter and the Sea Level Table (on page 39) to find the Uncorrected D.O. Value
2. Use your location's altitude and the Correction Chart on this page to find the corresponding correction value.
3. Multiply the uncorrected D.O. value from step 1 by the correction value from step 2 to get the Corrected D.O. value.
4. The value calculated in step 3 (Corrected D.O. value) and the value displayed on the meter should be within +/- 0.5 mg/L of each other.

APPENDIX E. DISSOLVED OXYGEN MAINTENANCE TIPS AND DETAILS FOR POLAROGRAPHIC PROBES

DO Membrane and Electrolyte

Erroneous reading will result from loose, wrinkled, torn, or fouled membranes, from bubbles in the electrolyte solution, or a lack of electrolyte under the membrane. Tiny holes in the membrane may be hard to see but will negatively affect performance. The following considerations are important for DO probes:

- Visually inspect membranes prior to each use
- NO tears, bubbles, wrinkles, or biological growth (white, green, black spots or fuzz) should be observed
- Rinse with distilled water after using to prevent biological growth
- Store in a moist, clean environment to prevent the DO membrane from drying out.
- Between sampling sites, the probe should be placed back in the calibration cup with a small amount of moisture (moist sponge, water droplets, etc.) or wrap a damp towel around the probe guard.

Changing membranes

Changing membranes will help reduce problems. Most manufacturers recommend changing the DO membrane at least once per month. The need to change membranes depends on usage, so inspect regularly. Change membranes as directed by the manufacturer. This is generally recommended in the following situations:

- When calibration is difficult or impossible
- When readings are erratic
- If meter frequently fails post-sampling check
- If membrane has dried out or is damaged (i.e. tears, wrinkles, bubbles, biological growth, dirty)

Calibrating after a membrane change

Most manufacturers recommend allowing stretch-on membranes to relax overnight (6-8 hours) prior to calibration. If conditions necessitate using the sensor and new membrane before the recommended overnight conditioning time, more frequent calibration drift checks and possibly recalibration are necessary for accurate DO measurements.

NOTE: *The overnight relaxation time applies only to stretch-on membranes, not cap membranes.*

Anode and cathode condition

Clean the anode and cathode as recommended by the manufacturer. Depending on probe usage and conditions, deposits (generally black spots of silver chloride (AgCl)) will form on the anode and cathode. These deposits will reduce the sensitivity of the probe. Refer to the instruction manual or consult the manufacturer for the proper cleaning procedure. Cleaning instructions generally involve lightly buffing the gold cathode and either sanding of the silver anode with 400 grit sandpaper or soaking it in dilute ammonium hydroxide solution.

APPENDIX E (CONT'D). DISSOLVED OXYGEN MAINTENANCE TIPS AND DETAILS FOR POLAROGRAPHIC PROBES

Proper Calibration and Measurement Conditions

Erroneous readings may result in the following situations:

- The probe is calibrated or the calibration drift check is performed under improper conditions, which include:
 - water droplets on the membrane or temperature sensor
 - unstable temperature (instability greater than 0.5 °C)
 - pressure in the calibration cup is not equal to ambient pressure (calibration cup not vented to atmosphere)
 - Entering an inaccurate or barometric pressure during calibration
 - Not having the proper altitude or barometric pressure for performing the calibration check

- The meter is used improperly when taking a measurement.

NOTE: Sufficient water movement across the probe face is required. This is generally 6 to 12 inches unless the probe has a circulator or is engineered for reduced flow dependence.

APPENDIX F. pH MAINTENANCE TIPS AND DETAILS

Lack of electrolyte or old electrolyte

pH probes may have refillable reference electrode reservoirs or sealed, non-refillable reference electrode reservoirs.

- Non-refillable pH probes will need to be replaced periodically. For instance, the pH probes from YSI have a shelf-life of approximately 18-24 months. In general, YSI probes should be replaced about every 2 years. Consult the manufacturer for diagnostic procedures to check the lifespan of the probe.
- Refillable pH probes should be checked frequently to ensure electrolyte is at a suitable level and that no excessive crystallization is present. Excessive crystallization may prevent proper electrolyte flow. If crystallization is observed in the electrode, clean per the manufacturer's instructions.

Clogged reference junction

The reference junction must be able to allow contact between the sample and the reference solution within the probe. A blocked reference junction will produce erroneous measurements. All personnel using the meter should be aware of the location and condition of the reference junction. A black reference junction often indicates that cleaning is required. Follow the manufacturer's instructions for cleaning or replacing the junction.

Dirty or scratched pH bulb

The glass on the pH bulb is very fragile and must be protected. The glass bulb should be clear. A whitish or oily film is indicative of a dirty bulb. Slow response time often indicates that the glass bulb is dirty. Follow the manufacturer's instructions for cleaning the glass bulb. A scratched bulb often results in jumpy, erratic, or impossible readings. Scratched bulbs generally require replacement of the entire probe.

Improper storage

Follow the manufacturer's instructions for probe storage. Most manufacturers recommend storing the pH probe in pH 4 or pH 7 buffer. Never store a pH probe in distilled water. This allows ions to leach out from inside the probe. To restore a pH probe that had been stored in distilled water, most manufacturers recommend soaking the probe in pH 4 buffer. At least several hours to overnight soaking are typically required for restoration.

APPENDIX G. CONDUCTIVITY MAINTENANCE TIPS AND DETAILS

Conductivity Cell Condition

A clean conductivity cell is one of the most important requirements for obtaining accurate measurements. Rinsing with deionized water after each use is recommended. Follow the manufacturer's instructions for cleaning the conductivity cell. General cleaning instructions may include:

- Rinse the conductivity cell frequently with deionized water.
- Pay diligent attention that no dirt or debris remains inside the conductivity cell.
- Cleaning the cell with a q-tip or soft-bristled brush and isopropyl alcohol or a mild detergent. For more resistant residues, check the manufacturer's instructions.

Zero Check Point

A dry conductivity cell should read 0 in air. High quality distilled water has a conductivity in the range of 0.5 to 3 $\mu\text{S}/\text{cm}$. Performing a check of the conductivity cell in dry air is a good way to quickly check the zero point of the meter. If the meter does not read 0 in air, it should be cleaned thoroughly. If the meter will not read close to 0 in air after extensive cleaning, and will not calibrate or pass the low level check, it may need repair or replacement.

Improper Calibration or Measurement Procedure

For new users, improper calibration or measurement procedures are a common source of error. The two most common mistakes are:

- **Not fully submersing the probe:** Artificially low readings will result if the probe is not fully submerged.
- **Bubbles trapped inside cell:** Air bubbles trapped inside the cell may give erroneous readings. The enclosed, tubular design of some conductivity cells often trap air bubbles that the user cannot see. Gently agitate the probe to remove any air bubbles that may be trapped in the cell.

Failed Conductivity Checks

If the meter fails the conductivity check, rinse the cell repeatedly with deionized water, dry, and ensure the probe reads close to zero in air. Then repeat the check in fresh standard. A few reasons why a check might fail are: 1.) an initial bad calibration; 2.) contaminated standard; 3.) improper technique; or 4.) dirty conductivity cell.

APPENDIX H. DIRECTOR'S MEMO REGARDING METALS MONITORING SUSPENSION



Michael F. Easley, Governor
William G. Ross Jr., Secretary
North Carolina Department of Environment and Natural Resources
Coleen H. Sullins Director
Division of Water Quality

March 18, 2008

MEMORANDUM

To: Jimmie Overton
Regional Surface Water Quality Supervisors
Kent Wiggins
Rick Shiver

From: Coleen H. Sullins 

Subject: Continued Suspension of Routine Ambient Data Collections for metals

On April 3, 2007, DWQ Division Director Alan W. Klimek temporarily suspended the collection of routine total recoverable metals as part of the DWQ Ambient Monitoring System. This suspension also included a suspension of required total recoverable metals samples collected by Memorandum of Agreement with the NC NPDES Discharger Monitoring Coalitions (Memorandum April 3, 2007 attached).

DWQ has made significant progress in reviewing our metals water quality assessment techniques, evaluation criteria, and relevant standards. DWQ recognizes the potential significance of modernizing our water quality standards for metals on environmental assessments and the NPDES regulated community. By this Memorandum, I am therefore continuing the April 3, 2007 suspension for routine ambient data collections for metals as we develop an appropriate modification of our water quality standards.

Questions regarding special circumstances or special studies requiring continued monitoring of ambient surface waters should be directed to Jay Sauber at 919-743-8416. Questions on water quality standards for metals should be directed to Connie Brower at 919-733-5083 ext 380.

Cc: Chuck Wakild
Paul Rawls
Alan Clark
Ted Bush
Jay Sauber
Connie Brower



North Carolina Division of Water Quality 1617 Mail Service Center Raleigh, NC 27699-1617 Phone (919) 733-7015 Customer Service
Internet: www.ncwaterquality.org Location: 512 N. Salisbury St. Raleigh, NC 27604 Fax (919) 733-2496 1-877-623-6748

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APPENDIX H (CONT'D). DIRECTOR'S MEMO REGARDING METALS MONITORING SUSPENSION



Michael F. Easley, Governor

William G. Ross Jr., Secretary
North Carolina Department of Environment and Natural Resources

Alan W. Klimek, P.E. Director
Division of Water Quality

April 3, 2007

MEMORANDUM

To: Jimmie Overton
Regional Surface Water Quality Supervisors
Rick Shiver
Kent Wiggins

From: Alan W. Klimek 

Subject: Suspension of Routine Ambient Data Collections For Metals

Based on discussions with Senior DWQ managers, I am temporarily suspending the collection of total recoverable metals as part of the DWQ Ambient Monitoring System. This includes a suspension of required total recoverable metals samples collected by Memorandum of Agreement with the NC NPDES Discharger Monitoring Coalitions. This decision will not change any requirements for other components of NPDES permits. No changes to effluent or instream monitoring requirements in individual NPDES permits will be affected. This is not a permanent suspension of ambient metals collections. DWQ is conducting a review of our water quality assessment techniques, evaluation criteria, and relevant standards. We are also collecting new ambient data pertinent to this review. Upon completion of this review, the resumption of metals collections will be considered.

I find that ambient total recoverable metals are an ineffective indicator of toxic impacts on aquatic life. I have considered many issues in making this decision including the changing uses of our water quality standards and the changing scientific approaches used to establish appropriate water quality criteria. We will continue to evaluate new approaches to collect more meaningful information for evaluating the impacts of metals on aquatic life. We will incorporate these new approaches into our ambient monitoring program as soon as feasible. I will re-evaluate this suspension within one year and at that time the suspension will either be continued or monitoring programs will be altered to a more meaningful evaluation of metals impacts on aquatic life.

These issues are not unique to North Carolina. Many states, the EPA, and other interested groups are adapting to new scientific information concerning the best possible evaluation techniques for understanding the toxic affects of metals on aquatic life. This action is prompted by complex CWA 303(d) listing issues and our current understanding of the impacts of metals on aquatic life. Changes from total to dissolved forms and complex scientific issues have been incorporated in the most recent publications from the US EPA concerning the Biotic Ligand Model for Copper (<http://www.epa.gov/waterscience/criteria/copper/2007/criteria200702.pdf>) and the March 2007 EPA Framework for Metals Risk Assessment. These EPA publications identified critical scientific issues that need addressing including consideration of the various properties of metals and additional key environmental chemistry parameters that control the toxic properties of metals <http://www.epa.gov/OSA/metalsframework/>.

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Internet: www.ncwaterquality.org Location: 512 N. Salisbury St. Raleigh, NC 27604 Fax (919) 733-2496 1-877-623-6748

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APPENDIX H (CONT'D). DIRECTOR'S MEMO REGARDING METALS MONITORING SUSPENSION

Suspension Of Routine Ambient Data Collections For Metals
April 3, 2007
Page 2

Questions regarding special circumstances or special studies requiring continued monitoring of ambient surface waters should be directed to Jay Sauber. Questions on water quality standards for metals should be directed to Connie Brower.

Cc: Coleen Sullins
Paul Rawls
Alan Clark
Ted Bush
Jay Sauber
Connie Brower

APPENDIX I. NPDES COALITION FIELD MONITORING CHECKLIST

| | | | | |
|---|--|------------------------------|------------------------|-----------|
| Date of visit: | | | | |
| Field Monitor Information | | DWQ Staff Information | | |
| Name: | | | Name: | |
| Position title | | | Position Title: | |
| Laboratory: | | | Name: | |
| Certification #: | | | Position Title: | |
| Coalition: | | | | |
| Date of last field visit: | | | | |
| METER INFORMATION | | | YES | NO |
| Parameter(s): _____ | | | | |
| Model: _____ | | | | |
| Serial #: _____ | | | | |
| METER MAINTENANCE AND CALIBRATION | | | YES | NO |
| Is meter(s) in good working order and appears to be well-maintained (reasonably clean and undamaged)? | | | | |
| What is the typical maintenance schedule (ask monitor to describe) | | | | |
| How does the lab keep track of meter maintenance? | | | | |
| What is the planned response in the event of meter failure? (For instance, is a back-up meter and/or minor maintenance parts available) | | | | |
| Is an initial calibration performed at the beginning of the workday? | | | | |

| METER MAINTENANCE AND CALIBRATION | YES | NO |
|--|------------|-----------|
| Are meters and probes inspected before calibration? <ul style="list-style-type: none"> • pH: Condition of glass; color/condition of reference junction; electrolyte at proper level with no bubbles or crystals (refillable) • DO: DO membrane intact, no bubbles, wrinkles, or tears • Sp. Cond: Conductivity cell clean, free of debris | | |
| Are meters at a stable temperature when calibrated? | | |
| Is sufficient time allowed for DO probe stabilization before calibration? | | |
| Describe calibration procedure for DO, conductivity, and pH. | | |
| Describe any calibration verifications that are performed. Are calibration verification readings recorded (time, meter reading under calibration conditions, and post-calibration reading (if applicable))? Request that the completed calibration sheet for the sampling event be faxed to be included with this audit lists. | | |
| Explain how possible anomalous readings are identified and the response actions. | | |
| SAMPLING METHODS | YES | NO |
| Do sampling locations match official station descriptions and lat/longs? (Record GPS readings for the latitude and longitude for each site and attach a copy to this field audit checklist) | | |
| Does all sampling equipment appear to be clean and in good working condition? | | |
| Can the monitor visibly assess the site condition when sampling (i.e. light sufficient to ensure field parameter measurements and samples taken at appropriate depth; light sufficient to visibly assess stream condition)? | | |
| Are notes made regarding environmental conditions such as precipitation, weather, presence of trash, water condition, etc. | | |
| If sampled from a bridge or dock, are samples/measurements taken on the upstream side of bridge? If not, describe why. | | |
| If sampled from the bank, what methods are used to ensure samples/measurements are taken in main stream flow? (For instance, a sampling pole might be used). | | |
| Are locations sampled in a consistent location on all sampling events? For instance, is the sample always collected on the same side of a bridge or at the same bank location? | | |
| Are samples/measurements taken from a representative point in the waterbody ? (i.e. main channel, well-mixed, moderate flow, outside of mixing zones, etc.) | | |
| For sampling locations on private property, does the monitor have property owner's permission to access the sample locations? | | |

| SAMPLING METHODS | | |
|---|--|--|
| Are field measurements (DO, pH, conductivity, temp.) taken <i>in situ</i> ? If not, state which parameters are not and how they were taken. | | |
| Are the appropriate units of measurement used with field parameter readings (i.e. either printed on the field sheet or recorded by the sampler) | | |
| <p>Were analytical samples for lab analysis collected and preserved properly?</p> <p><u>TSS/Turbidity:</u></p> <ul style="list-style-type: none"> • Grab samples? <p><u>Fecals:</u></p> <ul style="list-style-type: none"> • Grab samples taken in sterilized container? • Sodium thiosulfate & EDTA as preservative? <p><u>Chl a:</u></p> <ul style="list-style-type: none"> • Photic zone or grab sample? • Brown opaque bottles? <p><u>Nutrients:</u></p> <ul style="list-style-type: none"> • Photic zone or grab sample? • 25% H₂SO₄ to pH<2 as preservative? <p><u>Metals:</u></p> <ul style="list-style-type: none"> • Standard grab or clean metals sampling / low level Hg sampling? • 1+1 HNO₃ to pH<2 as preservative ? • Low level Hg: Borosilicate glass, Teflon lined cap? 1+1 HNO₃ to pH<2 <p>Describe any deviations from above.</p> | | |
| <p>INTERMEDIATE SAMPLING DEVICE:</p> <ul style="list-style-type: none"> • If an intermediate bottle-holding sampling device was used, what type was it? • Is it made of non-reactive materials to reduce risk of contamination of samples? • If the sampling device is not a commercially available device (such as one constructed by the lab), take a picture and keep with completed field sheet. | | |
| <p>LABLINE:</p> <p>Was a labline used to collect a photic zone sample? If so, describe the procedure, including:</p> <ul style="list-style-type: none"> • Secchi disk use to measure photic zone • Sample collection throughout the depth of 2X photic zone • Cleaning of Labline before and after use <ul style="list-style-type: none"> --Rinsed with site water before use? --Rinsed with distilled water between uses? | | |
| Were any QC samples collected or QC procedures performed (Besides calibration checks on meters)? If yes, record sample information in comments. | | |

| SAMPLE STORAGE and TRANSPORT: | YES | NO |
|---|------------|-----------|
| Were samples placed in a cooler with ice within 15 minutes for transport? If not, describe why or which samples. | | |
| Were containers stored in a way to minimize possible contamination? (This may include placing samples in bags before placing on ice, placing samples on ice with lids above iceline, draining melted icewater frequently) | | |
| If low level Hg collected, was it double-bagged in a low-level Hg-only cooler? | | |
| Is a temperature blank included in each cooler? If not, describe how lab checks temperature of samples upon receipt. | | |
| How were samples transported to lab(s)?. | | |
| Will samples be received at lab within appropriate holding time? <ul style="list-style-type: none"> • Fecal coliform: 6 hours • Chlorophyll: 24 hours • Turbidity: 48 hours | | |
| Is a record of date collected, time collected, sample collector, and use of proper preservatives maintained (either by Chain of Custody or other system)? | | |
| SAFETY | YES | NO |
| Describe safety devices available and safety precautions taken. These may include: <ul style="list-style-type: none"> ○ Truck work: orange safety vest, flashing beacon, traffic cones ○ Boat work: PFD, whistle/air horn, paddles/oars, flare kit (coastal areas only), marine radio or cell phone (coastal areas only) ○ Acid handling equipment (safety glasses, gloves, spill kit, ampule disposal container, portable eyewash) ○ First aid kit (in vehicle) ○ Fire extinguisher (in vehicle) ○ Gloves to protect sampler from environmental contaminants | | |
| Are chemicals handled and discarded appropriately? NOTE: <i>Used calibration reagents should be poured into a secondary container to be discarded down a sink.</i> | | |