

Standard Operating Procedures for Non-tidal Monitoring (Tier I and Tier II)

Integration of Citizen-based and Nontraditional Monitoring into the Chesapeake Bay Program Partnership

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Acknowledged Works

Much of the information in this manual has been adapted from the following methods manuals:

Alliance for the Chesapeake Bay. 2012. Citizen Monitoring Program Manual

EcoCheck. (2013). Sampling and data analysis protocols for Mid-Atlantic non-tidal stream indicators. Wicks EC, Fries AS, Kelsey RH, (eds). IAN Press, Cambridge, Maryland, USA.

Alliance for Aquatic Resource Monitoring. 2013. Antietam Watershed Association Water Quality Monitoring Manual

Virginia Citizen Water Quality Monitoring Program. 2007. Virginia Citizen Water Quality Monitoring Program Methods Manual

Center for Marine Conservation & U. S. EPA. Volunteer Estuary Monitoring: A Methods Manual, Second Edition.

U.S. EPA. 1997. Volunteer Stream Monitoring: A Methods Manual. EPA 841-B-97-003.

U.S. EPA. 1996. Recommended Guidelines for Sampling and Analyses in the Chesapeake Bay Monitoring Program. EPA 903-R-96-006.

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1 Before You Begin

1.1 Safety, Equipment List, and Volunteer Responsibilities

1.1.1 Safety – General Precautions

- a) Always perform water-monitoring activities under the guidance of an adult.
- b) Read all instructions to familiarize yourself with the test procedure before you begin. Note any precautions in the instructions.
- c) Keep all equipment and chemicals out of the reach of young children and pets.
- d) Avoid contact between chemicals and skin, eyes, nose and mouth.
- e) Read the label on each reagent container prior to use. Some containers include precautionary notices or antidote information on the back of the container.
- f) In the event of an accident or suspected poisoning, immediately call the Poison Control Center phone number in the front of your local telephone directory or call your physician. Be prepared to give the name of the reagent in question and its code number. Most kit reagents are registered with POISINDEX, a computerized poison control information system available to all local poison control centers.

1.1.2 Protect Yourself & Your Equipment: Use Proper Technique

- a) Wear safety goggles or glasses when handling reagent chemicals.
- b) Use the test tube caps or stoppers, not your fingers, to cover test tubes during shaking or mixing.
- c) When dispensing a reagent from a plastic squeeze bottle, hold the bottle vertically upside-down (not at an angle) and gently squeeze it (if a gentle squeeze does not suffice, the dispensing cap or plug may be clogged).
- d) Wipe up any reagent spills, liquid or powder, as soon as they occur. Rinse area with a wet sponge, and then dry.
- e) Thoroughly rinse test tubes before and after each test. Dry your hands and the outside of the tubes.
- f) Tightly close all reagent containers immediately after use. Do not interchange caps from different containers.
- g) Avoid prolonged exposure of equipment and reagents to direct sunlight. Protect them from extremely high temperatures. Protect them from freezing.

1.2 Monitor Responsibilities

Choose a regular sampling day: Choose a convenient day of the week for sampling. Samples should be taken at regular weekly or monthly intervals. If it is not possible to sample on the same day each week, try to sample within 2 days (either side) of your regular day spacing the sampling dates, 5 to 9 days apart. Sample at the same time of day each week; if you are sampling multiple locations, be sure to always sample your sites in the same order each monitoring run to achieve similar sample timing.

Record your test results: Record data on a data collection form provided. Always record the test results as you go along. Keep a copy of the data collected for your records and to provide a backup copy should the original be lost.

Provide comments as necessary: The "Comments" section can be used to record general observations about the site especially changes due to erosion, recent notable weather, and any problems you had with the sampling procedures.

Submit data to database: If you have access to the internet, submit your data to the project's online database.

Send datasheets once every three months. Mail the data sheets to the Alliance or your Watershed Coordinator every three months so that we can maintain a current database.

Stay certified: Attend a recertification session every other year to maintain your skills and learn new information and techniques. You can also attend any training session to refresh yourself of the concepts and procedures between re-certifications.

2 QA/QC Procedures

2.1 Certification and Re-certification

2.1.1 Certification

All monitors that wish to submit Tier II data must gain monitor certification. Monitors can become certified at their initial training session by demonstrating a mastery of the sampling procedures and complete understanding of the quality assurance protocols used during data collection to be assessed by a Project Team member or Certified Trainer. Monitors must also pass a test that assesses the monitor's understanding of QA/QC procedures outlined in this SOP and the project QAPP with a 90% score.

Monitors that attend an initial training and are unable to pass the requirements to become certified at the end of the training will be encouraged to continue practicing their monitoring procedures. Un-certified monitors are encouraged assist a certified monitors in the field until they have become comfortable with the procedures and QA/QC protocols. Un-certified monitors are allowed to retake the certification test, and demonstrate proper sampling and analysis technique up to three times in order to become a certified monitor.

When a monitor achieves certification, they may be assigned a site and begin to collect Tier II data and submit it to the project database.

2.1.2 Re-certification

The Project Team and Certified Monitors will host recertification sessions biennially for monitors that have passed the initial training and wish to maintain their certification. Recertification sessions are conducted in a fashion that is similar to a lab practical. Monitors are checked to assure that: they remain proficient in methodology and understanding of basic water quality parameters; their equipment is operational and properly calibrated / verified; and they have an adequate supply of viable chemicals, procedures, equipment verification/check, and updated information about monitoring.

The recertification session is set up with a "station" for each water quality parameter. Monitors perform the test and compare their results to a known or controlled result. Project staff observe the monitors' methods and ensure that monitors correctly perform the tests and accurately record the data. After completing and "passing" one parameter, the monitor moves through each of the other stations while completing a datasheet that serves as documentation of re-certification. Replacement equipment, datasheets, information, and chemicals are given if needed. Alliance for the Chesapeake Bay retains documentation of recertification sessions.

2.1.3 Field Audits

Project Team members, the QC manager, or Certified Trainers may accompany monitors in the field and observe field collection procedures as part of the recertification process for monitors. Monitors will demonstrate proper sample collection, analysis, labelling, and preservation in accordance with this SOP.

2.2 Pre-monitoring checks

2.2.1 Equipment Check

Prior to going out into the field, monitors should check their equipment for cleanliness, breakage, probe function and battery life, and chemical expiration dates. If a monitor finds that their equipment is damaged and will affect the quality of the data they collect they will not collect data that day and mark the reason on their data sheet. The monitor should contact their Project Team member to get the equipment repaired or replaced prior to the next scheduled sample.

Monitors measuring dissolved oxygen using the Winkler titration will check the viability of their sodium thiosulfate solution prior to each monitoring event and record the results on their field datasheet. Sodium thiosulfate is used for monitoring dissolved oxygen. By using a standard solution of iodate-iodide, with 10 mg/L dissolved oxygen value, the monitor must record a value of 9.4 – 10 mg/L with their sodium thiosulfate measurement.

If results of the first check are above or below these intended values, a second check is performed. If the second check yields unacceptable values or if the two checks are greater than 0.4 mg/L apart from each other, the monitor is instructed to abandon the dissolved oxygen test because the sodium thiosulfate is no longer viable. The monitor must replace all expired chemicals prior to sampling again.

2.2.2 Calibration

Monitors will calibrate any equipment that requires calibration prior to being used (within 24 hours of use), using standard solutions and following the manufacturer's instructions. Monitors will note on their data sheet that they calibrated their equipment.

After sampling, it is recommended that monitors check their probes against the standard solutions used for calibration to identify instrument drift. If pH is outside of +/- 0.20 units, DO is +/- 0.3 mg/L, or specific conductance is +/- 5% of verification standards, the data must be flagged and the probe must be assessed and fixed or replaced if needed.

Monitors record these calibration and verification values on their datasheet and values are entered into the online database.

Thermometers that are verified should be re-verified every year. Thermometers must be verified against the Alliance master precision thermometer that is annually verified against an NIST-traceable thermometer to 0.2° C.

2.3 Field QC

2.3.1 Duplicates

If monitors are using the Winkler titration method for measuring DO they will perform the dissolved oxygen test on the actual water sample in duplicate. Monitors are instructed to do a third titration if their two initial titrations differ by more than 0.6mg/L. The two closest values are recorded on the datasheet.

Monitors collecting samples for Tier II laboratory analysis will perform duplicate samples at least 10% of the time. Duplicates consist of either collecting a larger sample for mixing and splitting it between two containers or immersing sample containers side by side in the water at the same time.

2.3.2 Replicates

Monitors will perform replicate samples of all other parameters (DO using Winkler titration method must be done in duplicate each sample) 10% of the time. The quality control samples are prepared and analyzed for all parameters of interest. The field replicate data are used to determine the overall precision of the field and laboratory procedures.

2.3.3 Field Blanks

Monitors will perform blank samples 10% of the time for samples to be sent to a lab for analysis. Monitors will perform all field procedures including preserving the samples as required and taking to the lab for analysis using deionized water provided by the laboratory. Results from field blanks will be recorded and appropriately marked during database entry.

3 Field Monitoring Procedures

3.1 Field Sampling Procedures

3.1.1 Best Practices

- a) Use of protective gloves. Gloves serve a dual purpose: 1) protecting the sample collector from potential exposure to sample constituents and 2) minimizing accidental contamination of samples by the collector. Wearing protective gloves at all times while sampling is recommended. Latex or nitrile gloves may be used for common sampling conditions.
- b) Safety always comes first. All sampling should be conducted with the proper equipment and least amount of danger to field personnel.
- c) Permission must be obtained from landowners before entering private property.
- d) Care should be taken not to disturb the bottom when sampling. When entering a stream, always walk in an upstream direction.
- e) Surface water should always be collected facing upstream and in the center of main area of flow. Therefore, unless safety is an issue, samples should be obtained from a bridge or instream.
- f) Samples should be collected in the main flow representative of the stream you are monitoring (for small streams, this is usually mid-channel) just below the water surface, about 0.3 meters (1 foot) deep.
- g) Whenever possible, collect field measurements directly from the sample site, not from bucket. If the field parameters need to be measured in the bucket, collect water quality samples (nutrients, etc.) first before placing the multi probe instrument in the bucket.
- h) When there are obvious standing pools of water during low or no flow conditions, do not collect samples or field measurements. Make a note of this on the data sheet.
- i) When collecting bacterial samples:
 - i. DO NOT rinse the bacteria sample bottle before collecting the sample.
 - ii. If sample bottles contain a dechlorinating tablet (usually small white tablet) and you are collecting an unchlorinated sample, dump out the tablet before collecting the sample.
 - iii. Be careful not to insert fingers into the mouth of the container or on the interior of the cap.

3.1.2 Streambank and Instream Sampling

If possible, wade into the stream to collect the sample. If wading to the sample site, always proceed upstream to allow the flow of the water to push any disturbed sediment downstream of where you will be collecting the sample.

When sampling from the streambank, care should be taken to sample from an area that will most closely represent the entire stream. Typically, this will be the area of the greatest flow in the stream and away from stagnant pools or eddies.

Step	Bacteria Samples	Nutrient and Chlorophyll Samples
1.	Walk upstream to the sample location. Be sure any sediment or debris disturbed from your movement in the streambed is not present where you will collect the sample.	Walk upstream to the sample location. Be sure any sediment or debris disturbed from your movement in the streambed is not present where you will collect the sample.
2.	Submerge the container; neck first into the water. The mouth of the bottle should be completely below the water surface approximately 3-6 inches.	Lower the sample bottle so that one edge of the opening is just below the water.
3.	Invert the bottle so the neck is upright and pointing into the water flow.	Allow the bottle to fill to the neck of the bottle.
4.	Move the bottle forward away from the body for at least six inches.	Lift the filled container. Do not pour out any excess water.
5.	Return the filled container quickly to the surface. Pour any excess water and cap.	

3.1.3 Dock or Bridge Sampling

1. Sample in the center of main flow from or as close as you can get on the dock or bridge. If sampling from a bridge sample from the safest side of the bridge and where contamination is least likely to occur. Typically, sampling on the upstream side of the bridge or dock is less likely to be contaminated.
2. During rainy periods, avoid sampling where storm water runoff from the bridge can affect sample.
3. Obtain field parameters (DO, pH, temperature) first before lowering a sample bucket.
4. When lowering the sample bucket, allow it to fill ¼ the way full and retrieve. Swirl the contents and dump the rinse away from the sample location to avoid kicking up sediment.
5. Repeat step 4 two more times and on the final time fill ½ to ¾ the way full.
6. Retrieve the bucket and collect the samples in the following order.

1. Bacteria
 - Open the bottle without touching the inner wall of the bottle or lid.
 - Invert the bottle by holding to the main body of the bottle and lower into the bucket 3-6 inches.
 - Fill the bottle in a 'U' from the side of the bucket closest to you to the opposite end.
 - At the end, bottle opening should be facing up and remove from the bucket.
 - Pour off any excess water and cap with the lid.

2. Nutrients
 - Open the bottle and tilt so that one side of the bottle will be below the waterline of the bucket.
 - Allow the bottle to fill to the neck of the bottle.
 - Remove the bottle and cap. Do not pour off any excess sample.

7. In situations where field parameters must be obtained from the bucket, all water samples must be collected prior to inserting the probe in the bucket.

3.2 Air Temperature Measurement

Equipment: armored, digital thermistor, or probe

Temperature is reported in degrees Celsius (°C). Always measure air temperature before water temperature.

Method:

1. Locate a place near your site and hang the thermometer out of the direct sun.
2. Wait 3-5 minutes to allow the thermometer to equilibrate.
3. Record air temperature to the nearest 0.5 °C for the armored thermometer or to the nearest tenth of a degree for the digital thermistor or probe on Page 2 of the datasheet.

3.3 Recording General Observations

Record weather and general observations on the datasheet.

3.4 Water Clarity & Turbidity Measurement

3.4.1 Secchi Disk

Equipment: 8" Secchi disk with attached line

Method:

1. Remove sunglasses if you are wearing them and stand with the sun to your back. Try to lower the disk into a shaded area.
2. Lower the disk into the water until the disk barely disappears from sight. Note the depth reading, in meters, based on the length of line submerged. Each mark is one-tenth (or 0.1) meter.
3. Slowly raise the disk and record the depth at which it reappears (i.e. is barely perceptible).
4. Average the two depth readings obtained above. The average of the two readings is considered to be the limit of visibility, or index of transparency. Record this average to the nearest tenth of a meter on your data form.

3.4.2 Transparency Tube

Transparency tubes are a type of equipment used for measuring transparency of water in streams and rivers. They are helpful for measuring transparency in situations where the stream is too shallow for the Secchi disk to be practical and for running waters where flow is too fast that the Secchi disk cannot remain vertical. Sample water collected either directly from the stream or from the sampling bucket is analyzed.

Equipment: Transparency tube

Method:

1. Close the drain tube by squeezing the crimp.
2. Fill the transparency tube with your sample water. Water may be collected directly from the stream in the vicinity of the sampling location if the stream is too small to fill the bucket, or sample water collected in the sampling bucket may be used (See 5.4, "Collecting the Water Sample"). To collect water directly from the stream, point the top of the tube in the upstream direction and collect surface water, being careful not to disturb the stream bed. To analyze water collected in the bucket, pour sample water from the bucket water directly into the transparency tube.
3. While looking down through the opening of the tube, partially open drain crimp, slowly draw off sample (Control flow by squeezing the crimp).

4. When the black and white pattern begins to appear, immediately tighten the crimp.
5. Record the level of water remaining via the centimeter ruler on the side of tube.

3.4.3 Turbidity Kit

This test is performed by comparing the turbidity of a measured amount of the sample with an identical amount of turbidity-free water containing a measured amount of standardized turbidity reagent. The readings are made by looking down through the column of liquid at a black dot. If turbidity is present, it will interfere with the passage of light through the column of liquid. Small amounts of turbidity will cause a “blurring” of the black dot in the bottom of the tube. Large amounts of turbidity may provide sufficient “cloudiness” so that it is not possible to see the black dot when looking down through the column. Any color that may be present in the sample should be disregarded. This determination is concerned only with the haziness or cloudy nature of the sample.

Equipment: Turbidity kit – LaMotte 7519-01

Method:

1. Fill one Turbidity Column to the 50 mL line with the sample water. If the black dot on the bottom of the tube is not visible when looking down through the column of liquid, pour out a sufficient amount of the test sample so that the tube is filled to the 25 mL line.
2. Fill the second Turbidity Column with an amount of turbidity-free water that is equal to the amount of sample being measured. Distilled water is preferred; however, clear tap water may be used. This is the “clear water” tube.
3. Place the two tubes side by side and note the difference in clarity. If the black dot is equally clear in both tubes, the turbidity is zero. If the black dot in the sample tube is less clear, proceed to Step 4.
4. Shake the Standard Turbidity Reagent vigorously. Add 0.5 mL to the “clear water” tube. Use the stirring rod to stir contents of both tubes to equally distribute turbid particles. Check for amount of turbidity by looking down through the solution at the black dot. If the turbidity of the sample water is greater than that of the “clear water”, continue to add Standard Turbidity Reagent in 0.5 mL increments to the “clear water” tube, mixing after each addition until the turbidity equals that of the sample. Record total amount of Standard Turbidity Reagent added.
5. Each 0.5 mL addition to the 50 mL size sample is equal to 5 Jackson Turbidity Units (JTUs). If a 25 mL sample size is used, each 0.5 mL addition of the Standard Turbidity Reagent is equal to 10 Jackson Turbidity Units (JTUs). See Table 3.4-1 below. Rinse both tubes carefully after each determination.

Table 3.4-1-1. Turbidity Test Results – from LaMotte 7519-01 instructions

TURBIDITY TEST RESULTS			
Number of Measured Additions	Amount in mL	50 mL Graduation	25 mL Graduation
1	0.5	5 JTU	10 JTU
2	1.0	10 JTU	20 JTU
3	1.5	15 JTU	30 JTU
4	2.0	20 JTU	40 JTU
5	2.5	25 JTU	50 JTU
6	3.0	30 JTU	60 JTU
7	3.5	35 JTU	70 JTU
8	4.0	40 JTU	80 JTU
9	4.5	45 JTU	90 JTU
10	5.0	50 JTU	100 JTU
15	7.5	75 JTU	150 JTU
20	10.0	100 JTU	200 JTU

3.5 Water Temperature Measurement

Equipment: armored, digital thermistor, or probe

Method:

Surface Sampling:

1. Place your probe or thermometer 0.3 m beneath the surface of the water
2. Wait for the probe or thermometer to stabilize
3. Record your reading

Sample with bucket:

1. Hang thermometer in the bucket
2. Wait for the probe or thermometer to stabilize
3. Record your reading

3.6 Water Depth Measurement

Equipment: Secchi disk (for <3 m deep), or measuring tape with weighted end

Method:

1. At your sampling site, lower the measuring device into the water until it is resting on the bottom and the line is slack.
2. Record the depth reading, to the nearest tenth, based on the length of line submerged.

3.7 Dissolved Oxygen

3.7.1 Winkler Titration Method

Equipment: LaMotte Dissolved Oxygen Test Kit

Sodium Thiosulfate Check:

Prior to each sampling event (either the night before or the day of), you must run a test to make sure your Sodium Thiosulfate is still fresh and functional. Sodium Thiosulfate is fairly unstable and can degrade very suddenly, making it necessary to check it before each DO sampling. Perform this check at home before you go out. Here is how you do the check...

1. Rinse the titrating tube (small glass vial with plastic lid with hole in it) with a small amount of Iodate-Iodide Standard Solution (in large amber bottle).
2. Pour into waste container.
3. Repeat step 1 and 2 two more times
4. Pour 20 ml of the Iodate-Iodide Standard Solution into the rinsed titrating tube.
5. Add 8 drops of Sulfuric Acid (hold the bottle vertical to ensure equal drop size) to the 20 ml of solution and mix by swirling. Then place plastic cap (with hole in it) onto titrating tube.
6. Fill titrating syringe to the “0” mark with Sodium Thiosulfate.
7. Titrate using the Sodium Thiosulfate.
8. When solution turns a pale yellow color, but not clear:
 - a) Remove cap, leaving syringe in cap.
 - b) Add 8 drops Starch Solution (white bottle). Swirl titration sample gently to mix to a uniform blue color. Recap glass tube and continue titration process.
9. Continue adding Sodium Thiosulfate until solution turns from blue to clear.
10. Read results on syringe - Record your results under the Dissolved Oxygen portion on your field datasheet.
11. If results are less than 9.4 mg/l or greater than 10.0 mg/L, perform a 2nd test and record in the space on datasheet marked “2nd check”.
12. Dispose of solution in titrating tube and syringe by pouring down sink and flushing with additional tap water.
13. Keep the amber bottle solution at home- you don’t need to take into the field.

DO Sampling Method:

NOTE: Duplicate tests are run simultaneously on each sample to guard against error. If the amount of DO in the second test is more than 0.6 ppm different than the first test, you should do a third test. Record the average of the two closest results.

Since you will be doing two tests at the same time, thoroughly rinse both water sampling bottles with the sample water, filling and dumping the waste water downstream three times before collecting your sample.

1. Using the first sample bottle, submerge about 1/2 of the bottle opening allowing the water to gently flow into the bottle. Try to fill the bottle without causing a lot of bubbles. Submerge the filled bottle.
2. Turn the submerged bottle upright and tap the sides of the bottle to dislodge any air bubbles clinging to the inside of the bottle. Cap the bottle while it is still submerged.
3. Retrieve the bottle and turn it upside down to make sure that no air bubbles are trapped inside. If any air bubbles are present, empty the sample bottle downstream and refill. Fill the second sample bottle. Once two satisfactory samples have been collected, proceed immediately with Steps 4 & 5.
4. Place both sample bottles on a flat surface and uncap. While holding the bottle vertical, add 8 drops of Manganese Sulfate Solution followed by 8 drops of Alkaline Potassium Iodide Solution to each sample bottle. Always add the Manganese Sulfate first. Cap each sample bottle and mix by inverting gently several times. A precipitate will form. Allow the precipitate to settle to the shoulder of the bottle. Mix both bottles again and allow the precipitate to settle to the shoulder again.
5. Add 8 drops of the Sulfuric Acid both sample bottles. Cap the bottles and gently shake to mix, until both the reagent and the precipitate have dissolved. A clear-yellow to brown-orange color will develop. If brown flecks are present, keep mixing the samples until the flecks will not dissolve any further.

NOTE: Following the completion of Step 5, the samples have been "fixed," which means that dissolved oxygen cannot be added to the sample bottles. The titration procedure described in Steps 6-13 may be performed at a later time (but must be performed within 8 hours of sample collection). This means that several samples can be collected and "fixed" in the field and then carried back to a testing station for the remaining steps.

6. Pour 20 ml of the solution from one of the sample bottles into one of the glass tubes with a hole in its cap. Fill to white line so that the bottom of the meniscus (the curved surface of the liquid in the tube) rests on the top of the white line. The amount is critical so be sure to use the glass dropper to add or remove the sample solution from the tube. Place

cap on the tube.

7. Fill syringe (titrator) to the 0 mark with Sodium Thiosulfate solution. Be sure that there are no air bubbles in the syringe. Refer to kit manual for instructions on how to properly fill syringe.
8. To titrate the solution in the tube, insert the syringe into the cap of tube. Add 1 drop of Sodium Thiosulfate to test tube and gently swirl the glass tube to mix. Add another drop of the Sodium Thiosulfate and swirl the tube. Continue this process one drop at a time until the yellow-brown solution in the glass tube turns a pale yellow (lighter than the original yellow-brown solution but not clear). Once you reach this point, take the cap off while leaving the syringe in the cap.
9. Add 8 drops of Starch Solution to the glass tube. Swirl the tube gently to mix. The solution should turn from light yellow to dark blue.
10. Recap the glass tube and continue the titration process with the Sodium Thiosulfate remaining in the syringe (adding one drop at a time and swirling as described in Step 9), until the test tube solution turns from blue to clear. This is the endpoint. If the solution turns blue again, ignore it. Do not add any more Sodium Thiosulfate than is necessary to produce this first color change. Be sure to gently swirl the test tube after each drop.

NOTE: When the dissolved oxygen level is above 10 ppm, the solution in the tube will still be blue when the plunger tip of the titrator reaches 10 units. If it reaches this 10 unit line, do not go beyond that line. Usually, this will only happen when the water temperature is cold. In this case, refill the syringe to the 0 line from the Sodium Thiosulfate bottle and continue adding a drop at a time and swirling until reaching the endpoint.

11. Using the scale on the side of the syringe, read the total number of units of Sodium Thiosulfate used. Each line is 0.2 units. This number equals the number of parts per million (ppm) or milligrams per liter (mg/l) of dissolved oxygen in the water sample.
12. Carry out Steps 7-12 on second sample bottle and second glass tube.
13. Record the results of the two tests on the data sheet. If the difference between Test 1 and Test 2 is more than 0.6 ppm, you should do a third test and record the two results which are within 0.6 ppm.

NOTE: If using transparency tube to measure turbidity, perform this measurement now.

3.7.2 Electronic Probe Method

Equipment: Various models of dissolved oxygen probes and meters

Calibrating Dissolved Oxygen Probes and Meters

With practice and proper care for the DO probe, users can complete the entire DO probe calibration process within 5-10 minutes.

NOTE: Some probes may differ in displaying values. For DO probes, parts per million (ppm), and milligrams per liter (mg/L) are the same value. In addition, barometric pressure may be displayed in millibars (mBar) or in millimeters of mercury (mmHg).

Method:

1. Record the date of calibration. Calibration must be done each day you collect DO samples
2. Record the temperature of the probe just before you calibrate the probe
3. Set the barometric pressure (BP) mmHg or mBar- Most probes allow the user to adjust the barometric pressure readout of the probe for calibrating DO. The standard unit for barometric pressure is millimeters of mercury (mmHg) or millibars (mBar). You can get local barometric pressure readings from www.weatherunderground.com or www.noaa.gov. If using weather station data, it is important to adjust the reading by the altitude of the weather station. Appendix II explains how to calculate the correct reading.
4. Calculate the Theoretical DO Value mg/L- Prior to calibrating your probe, you should determine the theoretical DO value to confirm your probes readout. To determine the theoretical value, please follow the instructions found in Appendix II.
5. Record the mg/L reading of the calibrated DO level. If everything is working properly, the probe should display the correct DO level based on the altitude and temperature that you are calibrating at. The theoretical DO value and the probes calibrated readout should be within 0.2 mg/L. If not, try to recalibrate the probe or perform maintenance on the probe based on manufacturer instructions.
6. Turn off the probe if the manufacturer says so. If not, keep the probe on at all times while you are taking it out to the field and performing your field samples.

Measure DO

1. Place your probe 0.3 m beneath the surface of the water
2. Wait for the probe to stabilize, and then record your reading

Post Sampling Calibration Check

After the sample run is complete, return the probe to the calibration station to perform a quick post check. The post check consists of placing the probe in the DO calibration chamber and letting it equalize. This may take between 2 to 10 minutes depending on the condition of the probe.

1. Measure and record the temperature. If you did the morning calibration indoors, the probe temperature should be roughly close to the same as the morning calibration. If you are calibrating the probe outside, the temperature may be different from the earlier reading. This should not affect the post check.
2. Record the barometric pressure reading of the probe. This may have changed from the morning reading due to weather changes. You can get current local barometric pressure readings from the Internet. Remember to adjust any weather station data based on the instructions found in Appendix II.
3. As in the morning calibration, use Appendix II to determine your theoretical DO level.
4. Record the DO reading of the probe (ppm or mg/L). DO NOT recalibrate the probe. The purpose of this check is to see if the probe has drifted out of acceptable limits during the day.
5. Calculate the difference between the probe reported value and the theoretical DO value. If the probe is functioning properly there should be a difference of less than 0.50 mg/L from the afternoon theoretical DO level and the probe readout. If the calibration difference is greater than 0.50 mg/L the probe needs service and you must flag the data because the probe did not hold onto the calibration. If the calibration difference is 0.16 to 0.50 mg/L. The calibration of the probe is approaching the limits of accuracy and preventative maintenance may be required. It may be wise to clean the probe or replace the probe membrane when this occurs.

3.8 pH

3.8.1 Electronic probe method

Equipment: Various models of pH probes and meters

Calibration

The pH probe calibration procedure a similar protocol used in calibrating the DO probe. Most meters allow calibrating the pH probe using two different buffers. In most cases the use the 7.00 and 4.00 pH buffer solutions is suitable. If you are experiencing pH values above 7.00, calibrate using 7.00 and 10.00 buffer.

Use fresh buffer solution when you calibrate the probe and check the readings at the end of the day. If the probe is capable in doing so, please record the probe readings to the nearest hundredth unit place (Ex. 7.01) when performing the calibration.

1. Record the date of calibration. Calibration must be done each day you perform samples.
2. Record the temperature of the probe during calibration.
3. Record the probe reading as you place the probe in the 7.00 buffer solution. Gently swirl the buffer or the probe to obtain an accurate reading.
4. Calibrate the probe, the probe should now read a value close to 7.00 pH units. Most manufacturers of buffers provide a table showing the pH result that probes should display based on temperature. Check against this value displayed on the probe is close to this value.
5. Clean the probe with distilled or deionized water and blot dry
6. Immerse the probe in the 4.00 (or 10.00) buffer solution, record the stabilized value.
7. Calibrate the probe and it should now read a value close to 4 (or 10) pH units. Again, consult the buffer solution table to ensure accuracy.

After calibration, you may turn off the probe if the manufacturer says so. If not, the probe should be kept on at all times while going out into the field and prior to the post check. Follow manufacturer instructions regarding transporting of the probe into the field to prevent damage and drying out of the pH probe.

Field Sampling

IMPORTANT NOTE- When traveling to a sample station, keep the probe tip stored in the protective cap. This will keep the glass sensor hydrated.

1. Turn the probe on.
2. Dip the electrode about 2 to 3 cm either directly into the water or in your sampling bucket. Let the reading stabilize. This may take about 2 to 3 minutes.
3. Once the reading has stabilized record the reading on your datasheet.
4. Turn off the probe and replace the protective cap.

End of Day Calibration Check

To ensure the probe has maintained proper calibration, it is important to verify no significant probe drift has occurred. The procedures listed below will verify the probe did not drift outside QA/QC specifications. **DO NOT CALIBRATE** the probe during this check. Doing so will invalidate the data collected during the sample run.

1. Rinse off the probe and probe tip with distilled water and wipe dry using a soft cloth. Washing the probe will remove any material that may reduce probe life.
2. Place the probe into a container of pH 7.00 buffer. You may use the same buffer used during the morning calibration as long as the buffer was covered and appears clean.
3. Allow the probe to stabilize and record the temperature and pH reading in the “End of Day Temp C” and the “End of Day pH 7 Check” columns on the “pH Probe Calibration Form.”
4. Rinse the probe and repeat the end of day check process using the 4.00 or 10.00 buffer.

If both buffer checks are within 0.20 units from the calibration values, the probe is within specifications. If the readings are greater than 0.20 units, flag all pH data collected during the sample run by typing “pH probe flag” in the “Additional comments” section when entering data into the online database. Also note “pH probe flag” at the top of the hard copy datasheet. This is because sometime during the sample run, the probe exceeded QA/QC specifications.

3.8.2 Colorimetric Kit

Equipment: LaMotte or Hach pH kits

Method:

Look on the front of black box to determine whether you have a wide range pH kit or a narrow range pH kit (i.e. cresol red, phenol red, bromthymol blue, thymol blue).

1. Rinse one sample test tube and cap twice with water from the stream or bucket
2. Fill the sample test tube to the black line with water from the stream or bucket. The bottom of the meniscus should be even with the line. Use plastic dropper to add or

remove water from test tube.

3. For wide range pH kit, add ten drops of the wide range indicator while holding the reagent bottle completely upside down. For narrow range kits, add 8 drops of the indicator while holding the reagent bottle completely upside down.
4. Cap the test tube and mix the sample thoroughly.
5. Slide the tube in the comparator slot, hold it up to the sunlight, and record the pH value from the color in the comparator that most closely matches the sample tube color. When the color observed is between 2 colors on the comparator, the value is reported to the nearest 0.5 unit (for wide range kit) or 0.1 unit for other pH kits.

3.9 Salinity, Conductivity, and Total Dissolved Solids

Equipment: Various models of conductivity probes and meters

Calibration

Most probes that test for conductivity and TDS use a pre-made calibration solution with a specific conductivity value. The probe is immersed in the solution and calibrated to the value of the solution. It is good to use a calibration solution concentration similar to what you may find in the field to ensure accuracy.

1. Record the date of calibration. Calibration must be done each day you perform samples.
2. Record the temperature of the probe while you are calibrating the probe.
3. Write down the conductivity listed on the probe when you immerse the probe into the conductivity solution and record the value prior to calibration.
4. Record the conductivity solution that you will use to calibrate the probe. The standard unit for these solutions is in microsiemens per centimeter (mS/cm) but probes may use different units.
5. Write down the conductivity reading after you have calibrated the probe in the solution. The probe should be very close to the calibrated buffer solution but may be off by a couple of units.

Measure salinity, conductivity & TDS

1. Prior to sampling, rinse the probe with deionized or distilled water.
2. Select the appropriate mode and range on the meter, beginning with the highest range and working down. Some probes will auto select the correct range.
3. Place the probe into the sample water, and read the salinity, conductivity or TDS of the water sample on the meter's scale.

NOTE: If your probe does not automatically select the appropriate measurement range, and the reading is in the lower 10 percent of the range that you selected, switch to the next lower range. If the reading is above 10 percent on the scale, then record this number on your data sheet.

4. Rinse the probe with distilled or deionized water between each sample and before post sampling calibration check. Replace the cap for storage and transport.

Post sampling calibration check

1. Record the temperature of the probe at the end of the day when you are performing the calibration check.
2. Record the temperature of the probe at the end of the day when you are performing the calibration check.
3. Write down the conductivity listed on the probe when you immerse the probe into the conductivity solution and record the value.
4. Calculate the difference between the pre and post sampling calibration values.
5. Standard rule of thumb is if the probe difference is less than 10.00%, you should be confident of the probe values. To calculate the relative percent difference use the formula:

$$\text{RPD}\% = \frac{\text{AbsoluteValue}(\text{Sample1} - \text{Sample2})}{\text{Average}(\text{Sample1} + \text{Sample2})} \times 100\%$$

6. Initial the person calibrating and using the probe for your records. This is good to know in case something happens to the probe that you may not be aware of due to someone else is using it.

3.10 Nitrate – Nitrogen and Orthophosphate Kits

Equipment:

- Nitrate – Nitrogen kit w/ all chemicals and clean glassware (Hach NI-14 14161000, LaMotte, 3110, LaMotte 3354)
- Orthophosphate kit w/ all chemicals and clean glassware (Hach PO-19 224800, Hanna HI 38061, Hanna HI 713)
- Clean polypropylene sample bottle or scintillation vial (60 ml)

Method:

1. Rinse the sample bottle with sample water and dispose of downstream
2. Repeat step 1 three times.
3. Fill the bottle with sample water and cap. Process the sample as soon as possible.
4. Make sure the sample is well mixed prior to analysis by shaking the sample bottle.
5. Follow the protocol for each nutrient type as outlined in the instructions accompanying the kit. Reagents should be maintained at about 20° C to yield best results.
6. Record your results on the data sheet.

3.11 Alkalinity

Equipment: LaMotte 4491-DR-01, LaMotte 3467-01, or LaMotte 4533-DR-01

Method:

1. Rinse the sample bottle with sample water and dispose of downstream
2. Repeat step 1 three times.
3. Fill the bottle with sample water to the 5mL line.
4. Add an indicator tablet.
5. Cap and swirl the vial to mix until the tablet dissolves.
6. Fill the titration syringe with the titration reagent.
7. Insert the titrator syringe into the center hole of the test tube cap.
8. While gently swirling the tube, slowly press the plunger to titrate until the solution color changes from blue-green to purple. Consult the alkalinity endpoint color chart.
9. Read the test result directly from the scale where the large ring on the titrator meets the titrator barrel. Record as ppm on your data sheet.
10. Make sure the sample is well mixed prior to analysis by shaking the sample bottle.
11. Follow the protocol for each nutrient type as outlined in the instructions accompanying the kit. Reagents should be maintained at about 20° C to yield best results.
12. Record your results on the data sheet.

Equipment: Hanna HI 775 Digital Checker

Pre Sample Check:

1. Turn the meter on by pressing the button, all segments will be displayed. When the display shows ‘Add’, ‘C.1’ with ‘Press’ blinking, the meter is ready.
2. Fill the cuvette to the 10 mL line on the cuvette with unreacted sample and replace the cap. Place the cuvette into the meter and close the meter’s cap.
3. Press the button. When the display shows “Add”, “C.2” with “Press” blinking the meter is zeroed.

4. Wipe the standardized cuvette clean with a Kimwipe.
5. Place the standardized cuvette into the meter and close the meter's cap.
6. Press and hold the button until the timer is displayed on the LCD (the display will show the countdown prior to the measurement) or, alternatively, wait for 3 minutes and press the button.
7. Record your standard reading on your data sheet.

Method:

1. Turn the meter on by pressing the button, all segments will be displayed. When the display shows "Add", "C.1" with "Press" blinking, the meter is ready.
2. Fill the cuvette to the 10 mL line on the cuvette with unreacted sample and replace the cap. Place the cuvette into the meter and close the meter's cap.
3. Press the button. When the display shows "Add", "C.2" with "Press" blinking the meter is zeroed. Note: Any chlorine present in the sample will interfere with the reading. To remove the chlorine interference add one drop of HI 93755-53 Chlorine Remover to the unreacted sample.
4. Remove the cuvette, open it and using a 1 mL syringe carefully add exactly 1.00 mL of Alkalinity Reagent to the sample. Replace the cap and gently invert 5 times. Place the cuvette back into the meter. Note: Pay attention not to spill reagent otherwise full color development may be inhibited.
5. Press the button. The instrument directly displays the concentration of alkalinity in ppm of CaCO₃. Alkalinity conversion: 1 ppm CaCO₃ = 0.02 meq/L = 0.056 dKH The meter automatically turns off after 10 minutes.

3.12 Phosphate

Equipment:

- Hanna HI 713 Phosphate Low Range Checker
- Clean polypropylene sample bottle or scintillation vial (60 ml)

Pre Sample Check:

1. Turn the meter on by pressing the button, all segments will be displayed. When the display shows ‘Add’, ‘C.1’ with ‘Press’ blinking, the meter is ready.
2. Fill the cuvette to the 10 mL line on the cuvette with unreacted sample and replace the cap. Place the cuvette into the meter and close the meter’s cap.
3. Press the button. When the display shows “Add”, “C.2” with “Press” blinking the meter is zeroed.
4. Wipe the standardized cuvette clean with a Kimwipe.
5. Place the standardized cuvette into the meter and close the meter’s cap.
6. Press and hold the button until the timer is displayed on the LCD (the display will show the countdown prior to the measurement) or, alternatively, wait for 3 minutes and press the button.
7. Record your standard reading on your data sheet.

NOTE: If your standard value is outside ± 5 mg/L of the expected value, acquire a second standard to check the Digital Checker again. If the second standard is outside ± 5 mg/L of the expected value, replace the Digital Checker immediately and do not use for sample analysis.

Method:

1. Rinse the sample bottle with sample water and dispose of downstream three times.
2. Fill the bottle with sample water and cap. Process the sample as soon as possible.
3. Make sure the sample is well mixed prior to analysis by shaking the sample bottle.
4. Turn the meter on by pressing the button. All segments will be displayed. When the display shows “Add”, “C.1” with “Press” blinking, the meter is ready.
5. Fill the cuvette with 10 mL of unreacted sample and replace the cap. Place the cuvette into the meter and close the meter’s cap.
6. Press the button. When the display shows “Add”, “C.2” with “Press” blinking the meter

is zeroed.

7. Remove the cuvette from the meter and unscrew the cap. Add the content of one packet of HI 713-25 reagent. Replace the cap and shake gently for 2 minutes until the powder is completely dissolved. Place the cuvette back into the meter.
8. Press and hold the button until the timer is displayed on the LCD (the display will show the countdown prior to the measurement) or, alternatively, wait for 3 minutes and press the button.
9. The instrument directly displays the concentration of phosphate in ppm. The meter automatically turns off after 2 minutes.
10. Record your results on your datasheet.

3.13 Bacteria

Equipment: Coliscan Easygel Kit

Sample collection:

Note the amount of rainfall within 48 hours prior to sampling and record in the bacteria section of the datasheet.

Collecting by wading:

4. Wade into the main flow of the stream
5. Take a few steps upstream with minimal disturbance;
6. Un-cap the sterile and pre-labeled bottle without touching the inside of the lid
7. Using a U motion dip the bottle into the water down and away from yourself allowing the bottle to fill $\frac{3}{4}$ full.
8. Cap the bottle and place sample on ice in cooler immediately (cooler temperature should be 1°C to 4°C. NOTE: Do not freeze your sample.

Collecting using a bucket:

1. Make sure not to touch inside of bucket with your hands.
2. If sampling from a dock or pier, go as far as possible to the end of the pier to collect your sample.
3. Throw the bucket out as far as possible in the main channel, and try not to disturb the bottom.
4. Rinse the bucket three times with stream water collected downstream of your sampling location.
5. Fill the bucket with the sample water to $\frac{1}{3}$ full.
6. Un-cap the sterile and pre-labeled bottle without touching the inside of the lid
7. Using a U motion dip the bottle into the water down and away from yourself allowing the bottle to fill $\frac{3}{4}$ full.
8. Cap the bottle and place sample on ice in cooler immediately (cooler temperature should be 1°C to 4°C. NOTE: Do not freeze your sample.

Collecting using a sampling pole (from bridge or dock):

If sampling from a boat make sure that the boat motor has not stirred up the water. If the water is shallow, sampling should be done through wading.

1. Un-cap your sterile and pre-labeled bottle and secure it to the end of the pole.
2. Extend the pole outward and dip at approximately 0.3 m below the surface.
3. Cap the bottle and place sample on ice in cooler immediately (cooler temperature should be 1°C to 4°C. NOTE: Do not freeze your sample.

After sampling bacteria wash your skin that came in contact with the water with disinfectant or soap to reduce your chances of becoming sick.

Bacteria Sample Plating

Write the site designation, sample #, date, and time on the bottom of the Petri dish lid with a permanent marker. It is best to use small lettering on the outer rim of the dish.

1. Use proper technique to keep pipette sterile: open pipette packet bulb-side first so that you do not contaminate the tip.
2. Gently mix the water sample in the bottle. Pipette the desired volume (1.0 – 5.0 milliliters) of sample water directly into Coliscan media bottle. It is best to dispense 2-ml in two separate allotments for a total of 4 ml while using a 3 ml disposable pipette. Be careful not to let the bottle lid touch anything to prevent sample contamination.
3. Record the expiration date of the media bottle on your datasheet.
4. Gently mix (do not shake) bottle of Coliscan media containing the sample water, and then pour the entire contents into a Petri dish. Only open the Petri dish long enough to pour in the sample.
5. Gently swirl Petri dish so the Coliscan media covers the entire bottom. For safety purposes, tape the Petri dish shut at this point.
6. Allow the media to solidify for approximately 60 minutes prior to incubation. (Amount of time will vary based on room temperature.)
7. Put plates in incubator and try to maintain at 37°C (= 98.6°F) for 24 hours. If no incubator is available, place the dish in a safe warm place out of direct sunlight, such as on top of a fridge or a water heater. Depending on temperature, the plates may need to be incubated for

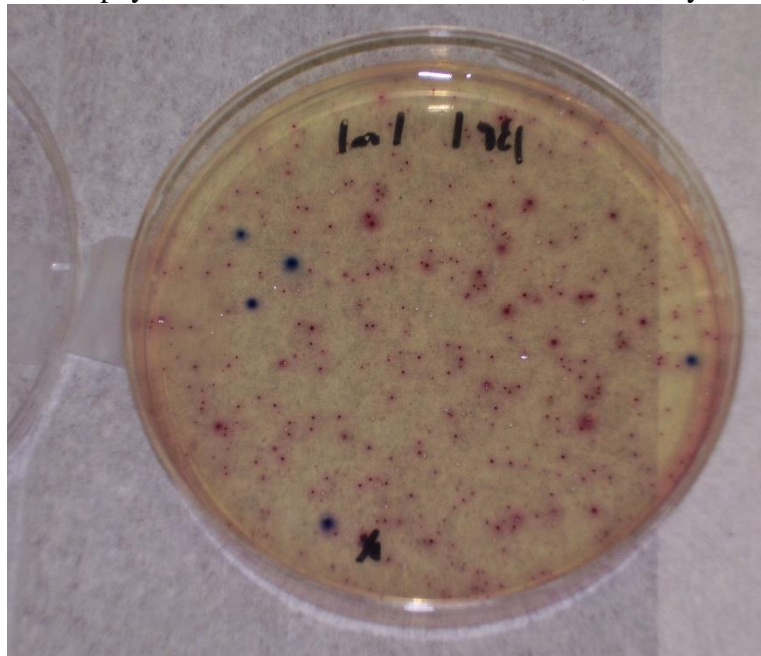
48 to 72 hours.

8. Record the average incubator temperature on the datasheet as well as the # of hours that the plates were in the incubator.

NOTE: As soon as plates are removed from incubator, they must be scored.

Bacteria Scoring

1. Place the Petri dishes on a white background or in natural sunlight. Count the number of dark blue (NOT TEAL) to purple (NOT PINK) colored colonies larger than pinprick size on each plate. Do not pay attention to halos around the dots, but only the center color.



2. Record this number in the column labeled “Total # of purple or dark blue colonies on plate” on the data form. Repeat for replicate #2.
3. Calculate the number of E. coli per 100 milliliters of water by following the instructions on the datasheet and record.
4. Calculate the average number of E. coli per plate and record on the datasheet. This is the value you will report in the online database.

Bacteria Monitoring Cleanup and Disposal

1. Throw used pipettes in the trash.
2. Rinse empty Coliscan bottles 2-3 times with tap water and dispose of in the trash can. (If media bottles are not rinsed, pathogens could grow in the remaining media.)

3. Add bleach or rubbing alcohol to each Petri dish to completely cover the solid media.
Allow dishes to stand for at least 10 minutes to ensure all bacteria have been killed.
4. Place the plates in a zip-lock bag and dispose of in the trash.

4 Lab sample collection preparation and handling

4.1 Nutrient and Grab Samples

Collecting from a boat:

1. Water samples should be taken one meter from the surface and one meter from the bottom of the water column at sites with depths greater than four meters. Because it is below the layer of mixing caused by wind, boating, and other activities, sampling one meter below the surface gives a better representation of the surface water column.
2. At sites with depths less than four meters, water samples should be taken one meter from the surface.
3. Facing upstream, extend the pole and bottle, rinse the bottle out three times, and take the sample the fourth time.
4. After samples are taken, immediately place the sample on ice up to the shoulders of the bottle. The lid should not be immersed under the ice, in case ice water leaks into the sample bottle, diluting the concentration of the sample.
5. On the field data sheet, record the time, date, and any other information about the water sampling event.

Collecting by wading:

1. Wade into the main flow of the stream
2. Take a few steps upstream with care not to disturb the sediment;
3. Un-cap the pre-labeled bottle
4. Using a U motion dip the bottle into the water down and away from yourself allowing the bottle to fill to the shoulder
5. After samples are taken, immediately place the sample on ice up to the shoulders of the bottle. The lid should not be immersed under the ice, in case ice water leaks into the sample bottle, diluting the concentration of the sample.

Collecting with a sampling pole:

1. Attach the sample bottle to the sampling pole, making sure that the clamp is tight.
2. The sampling point in the stream or river should have a low to medium flow and not be in eddies or stagnant water.

3. Facing upstream, extend the pole and bottle, rinse the bottle out three times, and take the sample the fourth time.
4. Fill the bottle up to the shoulders and immediately cap and place on ice. The lid should not be immersed under the ice, in case ice water leaks into the sample bottle, diluting the concentration of the sample.

4.2 Chemical preservatives and reagents

The nutrient sample bottles contain a small amount of sulfuric acid as a preservative. When sampling it is important to fill the bottle to the needed level and not pour out the preservative or excess sample from the bottle.

The bacteria sample bottle contains a dechlorinating tablet. When collecting non-chlorinated water, discard the tablet. Samplers should discard the tablet just prior to collecting a bacteria sample at the site. Discard the tablet by dumping out of the bottle without touching the lip or inner wall of the sample bottle. The tablets are harmless to the environment and may be left at the site.

4.3 Sample container handling and preservation

Proper sample containers and sample preservation are essential to sample integrity. Samples not preserved properly may be rejected by the laboratory.

- a) Sample containers should be inspected and any torn, punctured or cracked sample containers discarded.
- b) After collecting the sample, make sure the lids are secured tightly to prevent contamination from water seepage in or out of the container.
- c) Sample containers and coolers should be stored with the tops securely fastened. Containers with loose fasteners should be replaced or taped to prevent loss of sample containers during transport.
- d) In the field, unless specified otherwise, all samples should be placed in an ice filled cooler immediately after collection. To ensure samples do not exceed the 4°C holding temperature, sample containers shall be placed upright and if possible, covered with ice in such a manner that the container openings are above the level of ice. Bacteria sample bottles should be stored in bags, placed in coolers and surrounded with wet ice.
- e) Glass sample containers should be packed in bubble wrap or other waterproof protective materials to minimize accidental breakage.
- f) The laboratory will provide temperature bottles that they use to determine sample temperature upon arrival at the lab. Make sure that every cooler used to ship samples to the lab contains one of these bottles.

4.4 Sample Bottle Identification

Each sample container must include a label with the following information.

- a) Station ID or description
- b) Date and time of sample collection
- c) Collector's initials
- d) Sample depth in meters (surface samples are reported as 0.3)
- e) Parameter name and/or group code,
- f) Container number
- g) Preservative used and volume filtered, if applicable.

Samples will not be analyzed if this information is missing. If more than one container is needed for a parameter (such as a duplicate sample), each container collected for that parameter must have a label with identical information in addition to an indication of 1 of 3, 2 of 3, 3 of 3, etc., as required. Split samples should be designated as S1 and S2.

Please remember to fill out the labels on the bottle with a waterproof pen before taking the samples.

It is essential that the actual sampling site match the labeling information. Always check the labeling information against the actual site. Samples not labeled properly may be rejected by the laboratory.

4.5 Transport of Samples

After collecting the samples at the site:

1. Place the bottles in the cooler filled with ice. Coolers should have enough ice to come up to the necks of the sample bottles.
2. Place any chain of custody forms in the Ziploc bag taped to the inner lid of the cooler.
3. Transport the cooler with samples to the designated drop off point or laboratory by the specified time.

5 Lab Procedures

Lab work will be performed by a NELAP, federal, or state approved lab. The following are the approved methods and their corresponding SOPs for reference for laboratories. It is expected that laboratories will be in compliance with these methods and will already be in possession of the procedural documentation for these methods.

Parameter	Method	Appendix
Silicate	US EPA method 366.0	Appendix III
Nitrate - Nitrogen	USEPA Method 352.1	Appendix IV
Nitrite - Nitrate	USEPA Method 353.3	Appendix V
Ammonia - Nitrogen	USEPA Method 350.1	Appendix VI
Total Nitrogen	USEPA Method 351.2	Appendix VII
Total Phosphorus	USEPA Method 365.4	Appendix VIII

Laboratories will perform QA/QC measures including: method blanks, matrix spikes, replicates, check standard.

6 Cleanup and Storage of Water Monitoring Equipment

- a) Rinse the thermometer in tap water and store upright.
- b) Pour contents of DO sampling bottles and chemical kits into the sink. Rinse all the bottles and containers thoroughly with tap water. Put all equipment away until next sampling time.
- c) Store all chemical reagents in a dark, cool place and out of the reach of children and pets!
- d) Save expired chemicals and give them to your monitoring coordinator or trainer at the next recertification event for proper disposal.

NOTE: If you conduct the sampling procedures away from home or on a boat, you need a special container for safe disposal of the test samples. A plastic milk jug or jar works well and is easy to obtain. Fill this container about $\frac{1}{2}$ to $\frac{3}{4}$ full with kitty litter to absorb the moisture. When the litter is saturated, place the closed jar in double plastic garbage bags and dispose of in the trash.

6.1 Maintenance for pH meter

Follow maintenance and care guidelines as specified by the manufacturer manual. Below are some general day to day care tips.

1. Ensure the probe is cleaned and well maintained. After each sample run, rinse off the probe with distilled water. Use a soft cloth and gently dry the probe and glass sensor.
2. Store the probe tip in the cap provided by the manufacturer. Inside this cap, place a small cotton ball or piece of paper towel soaked with pH 4.00 buffer (or probe storage solution). This will keep the probe in working condition until the next field sampling event.
3. If you see any biological growth (mold, algae, etc.), use mild soap or warm (~30o C) pH 4.00 buffer to clean. Rinse with distilled water and dry.
4. If the calibration or end of day check indicates there is a problem with the probe, and standard cleaning does not produce acceptable results, replacement of the sensor cap may be necessary. Contact a Project Team Member to get a replacement sensor cap.

Appendix I

Field Data Sheet

Appendix II

Theoretical DO Calculation

How to Calculate Theoretical Dissolved Oxygen Values

From: Virginia Citizen Water Quality Monitoring Program Methods Manual - October 2007

Proper calibration of Dissolved Oxygen (DO) probes is important to collect accurate data. An easy way to see if a probe is calibrated correctly is to compare the probe's results against a theoretical DO value. This value is what the DO level should be based on temperature and barometric pressure.

DO Level based on temperature

The top table on the attached chart allows users to find the DO level based on temperature. The top and side axis of the table corresponds to the temperature that the probe is reporting. The intersection of the two axes displays the DO reading. Write this number down to start calculating the theoretical DO level.

Correction factor for barometric pressure

Barometric pressure is a way to tell how much atmosphere is pressing down on a surface. Weather systems and elevation above (or below) sea level can change this value. The bottom table of the attached chart will help compensate for these changes in pressure. Dissolved oxygen probes normally show pressure in millimeters of mercury (**mmHg**) or millibars (**mBar**).

Having a barometer on hand is a good way to get pressure data. A weather station can also provide pressure data. Websites such as www.weatherunderground.com are useful to find local weather stations. Please note that most barometers and weather stations report pressure in inches of mercury (**inHg**).

Note about using weather station pressure readings

Weather stations compensate pressure readings to make it appear as if the station is at sea level. To account for this, subtract the barometric pressure by 1.01 inHg per 1,000 feet in elevation of the weather station. This final value is known as **absolute barometric pressure**.

Example: Find the absolute barometric pressure of a station located 222 feet above sea level that reported 30.12 inHg.

$$30.12 \text{ inHg} - \frac{1.01 \text{ inHg}}{1000/222 \text{ feet}} \rightarrow 30.12 - \frac{1.01}{4.50} \rightarrow 30.12 - 0.22 == 29.90 \text{ inHg absolute barometric pressure}$$

Once finding the absolute pressure, use the bottom table found on the attached chart to find the proper correction factor to use. The formulas at the bottom of the chart will help in converting inHg barometric pressure readings into **millibars** (mBar) or **millimeters of mercury** (mmHg) that are commonly used to calibrate a dissolved oxygen probe. Use this value to find the correction factor to use in the final calculation.

Example: A barometric pressure of 970 millibars you would use a correction factor of 0.96 (second column, bottom row).

Theoretical DO Calculation

To find the theoretical DO value, use the following formula.

$$\text{Theoretical DO} = (\text{DO level based on temperature}) \times (\text{barometric pressure correction factor})$$

Example: If a probe had a temperature of 18.4 C and the barometric pressure was 970 mBar, the theoretical DO value would be 9.00 mg/L (9.37mg/L x 0.96 correction factor).

Dissolved Oxygen Saturation

Directions- To determine theoretical DO saturation, multiply the O₂ concentration value (found in the top chart) by the barometric pressure correction factor (bottom chart).

Example: Find the DO saturation for at a temperature of **18.4 C** at **730 mmHg** pressure: $9.37 \times 0.96 = 9.00 \text{ mg/L}$

Temp in °C	O ₂ concentrations in mg/l									
	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
5	12.75	12.71	12.68	12.65	12.61	12.58	12.55	12.52	12.48	12.45
6	12.42	12.39	12.36	12.32	12.29	12.26	12.23	12.2	12.17	12.14
7	12.11	12.08	12.05	12.02	11.99	11.96	11.93	11.9	11.87	11.84
8	11.81	11.78	11.758	11.72	11.69	11.67	11.64	11.61	11.58	11.55
9	11.53	11.5	11.47	11.44	11.42	11.39	11.36	11.33	11.31	11.28
10	11.25	11.23	11.2	11.18	11.15	11.12	11.1	11.07	11.05	11.02
11	10.99	10.97	10.94	10.92	10.89	10.87	10.84	10.82	10.79	10.77
12	10.75	10.72	10.7	10.67	10.65	10.63	10.6	10.58	10.55	10.53
13	10.51	10.48	10.46	10.44	10.41	10.39	10.37	10.35	10.32	10.3
14	10.28	10.26	10.23	10.21	10.19	10.17	10.15	10.12	10.1	10.08
15	10.06	10.04	10.02	9.99	9.97	9.95	9.93	9.91	9.89	9.87
16	9.85	9.83	9.81	9.79	9.76	9.74	9.72	9.7	9.68	9.66
17	9.64	9.62	9.6	9.58	9.56	9.54	9.53	9.51	9.49	9.47
18	9.45	9.43	9.41	9.39	9.37	9.35	9.33	9.31	9.3	9.28
19	9.26	9.24	9.22	9.2	9.19	9.17	9.15	9.13	9.11	9.09
20	9.08	9.06	9.04	9.02	9.01	8.99	8.97	8.95	8.94	8.92
21	8.9	8.88	8.87	8.85	8.83	8.82	8.8	8.78	8.76	8.75
22	8.73	8.71	8.7	8.68	8.66	8.65	8.63	8.62	8.6	8.58
23	8.57	8.55	8.53	8.52	8.5	8.49	8.47	8.46	8.44	8.42
24	8.41	8.39	8.38	8.36	8.35	8.33	8.32	8.3	8.28	8.27
25	8.25	8.24	8.22	8.21	8.19	8.18	8.16	8.15	8.14	8.12
26	8.11	8.09	8.08	8.06	8.05	8.03	8.02	8	7.99	7.98
27	7.96	7.95	7.93	7.92	7.9	7.89	7.88	7.86	7.85	7.83
28	7.82	7.81	7.79	7.78	7.77	7.75	7.74	7.73	7.71	7.7
29	7.69	7.67	7.66	7.65	7.63	7.62	7.61	7.59	7.58	7.57
30	7.55	7.54	7.53	7.51	7.5	7.49	7.48	7.46	7.45	7.44

Barometric Pressure Correction factor:

mmHg (mBar)	Corr. Factor	mmHg (mBar)	Corr. Factor	mmHg (mBar)	Corr. Factor	mmHg (mBar)	Corr. Factor
775-771 (1033-1028)	1.02	750-746 (1000-995)	0.987	725-721 (967-961)	0.953	700-696 (934-928)	0.92
770-766 (1027-1021)	1.014	745-741 (994-988)	0.98	720-716 (960-955)	0.947	695-691 (927-921)	0.914
765-761 (1020-1014)	1.007	740-736 (987-981)	0.973	715-711 (954-948)	0.94	690-686 (920-915)	0.907
760-756 (1013-1008)	1	735-731 (980-975)	0.967	710-706 (947-941)	0.934	685-681 (914-908)	0.9

755-751 (1007-1001)	0.993	730-726 (974-968)	0.96	705-701 (940-935)	0.927	680-676 (907-901)	0.893
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Appendix III

Laboratory Method – Silicate – US EPA 366.0

Appendix IV

Laboratory Method – Nitrate – Nitrogen – US EPA 352.1

Appendix V

Laboratory Method – Nitrite - Nitrate – US EPA 353.3

Appendix VI

Laboratory Method – Ammonia - Nitrogen – US EPA 350.1

Appendix VII

Laboratory Method – Total Nitrogen – US EPA 351.2

Appendix VIII

Laboratory Method – Total Phosphorus– US EPA 365.4

Appendix F:

ALLARM Specific Program Requirements

ALLARM Specific Program Requirements

A8.3 Certified Monitors

ALLARM monitors will be required to go through a recertification process once a year. The recertification process will include one of two options:


1. Certification Workshop: ALLARM will hold a Certification Workshop to recertify monitors. At the workshop, monitors will test known samples or external field duplicates will be tested by monitors and an ALLARM staff member.
2. Lab Analysis of Duplicate Samples: Monitors will send a duplicate sample to the ALLARM Community Aquatic Research Laboratory for comparison of results between the monitor and the ALLARM lab for each applicable parameter (alkalinity, conductivity, nitrate-nitrogen, orthophosphate, pH, total dissolved solids, and turbidity).

Each monitor will maintain their certification after completing and passing the recertification process above successfully. Passing criteria are met if the relative percent difference (RPD) between the results obtained by the monitor and the ALLARM staff/lab is $\leq 20\%$, or if the results fall within the accuracy range of the equipment.

A9.3 Other Documentation and Records

Monitors who send duplicate samples to the ALLARM Community Aquatic Research Laboratory for quality control/recertification will fill out an ALLARM Quality Control Form (Figure A9-1) and send it along with their water sample(s). Before a sample is analyzed in the lab, the monitor and sample information will be entered into the laboratory Quality Control binder (the monitor's results are not entered so there is no bias when recording the lab results). The same information, as well as the monitor's results will also be entered into a QC Excel spreadsheet that is maintained by ALLARM. The original Quality Control Forms will then be filed in the ALLARM office.

Figure A9-1. Example of a Quality Control Form used by monitors when submitting a duplicate water sample to the ALLARM Laboratory for analysis.



SHALE GAS VOLUNTEER MONITORING PROGRAM

Quality Assurance/Quality Control Form

1. Fill out the label on your QA/QC bottle.
2. Enter the stream and face upstream. Fill your QA/QC bottle and pour the rinse water out downstream. Rinse your bottle and cap three times. Fill your QA/QC bottle completely with stream water and close it tightly with the cap.
3. Record your results in the boxes below.
4. Fill out the information in the boxes below.
5. Pack a small box with your QA/QC bottle and this QA/QC form. Secure the bottle so it cannot move around during shipment. Mail the box to ALLARM for QA/QC processing at:

**ALLARM Shale Gas Volunteer Monitoring Program
Quality Assurance/Quality Control Bottle**

Monitor Name	
Stream Name	
Collection Date	
Bottle #:	

Parameter	Units	Replicate #1	Replicate #2	Average Result
Conductivity	µS/cm			
Total Dissolved Solids	mg/L			
Stage	feet			

Monitor Information		Sample Information	
Monitor's Name		Stream Name	
Mailing Address		Latitude Coordinate	
		Longitude Coordinate	
Email Address		Collection Date	
County Monitored		Collection Time	
Affiliation (if applicable)		Equipment Used (i.e. LaMotte meter)	

Alliance for Aquatic Resource Monitoring (ALLARM)

June 2013

B3.2 Samples collected for Quality Control

Samples that are collected for duplicate testing by the ALLARM Lab will be collected in 500 mL polyethylene bottles (provided by ALLARM), and labeled in the field with the monitor’s name, stream name, site name, and collection date and time. Monitors will collect samples following sample collection procedures in the CMC Non-Tidal Methods Manual (Appendix C). In the field, the samples are the responsibility of the monitor. The monitor will send the sample(s) along with their completed Quality Control Form to ALLARM (Figure A9-1) via mail or by dropping the sample(s) off at the ALLARM office. Most parameters will require refrigeration during the holding time, therefore monitors will place the sample(s) in an insulated box with frozen ice packs before shipping/delivering them to ALLARM. The Quality Control Form, Quality Control sample collection bottle, and shipping materials will be provided by ALLARM.

B4.1 ALLARM Analysis Methods of Duplicate Samples

Similar to the monitors, the ALLARM Lab will have a manual that contains detailed information on all of the sample handling, sample analysis, and data reporting protocols used for the analysis of duplicate samples sent by ALLARM monitors for quality control and recertification purposes. Table B4-1 summarizes a portion of this information.

Table B4-1. Summary of analytical methods used by the ALLARM Laboratory for analyzing duplicate samples.

WQ Parameter	Analysis Method #1 (Monitor Equipment)	Analysis Method #2 (Lab Equipment)
Alkalinity	Same as monitor (LaMotte 4491-DR-01, LaMotte 4533-DR-01, LaMotte 3467-01, Hanna HI 775)	Hach Spectrophotometer DR5000
Conductivity	LaMotte Tracer 1749	Fisher Scientific accumet XL200
Nitrate-nitrogen	Same as monitor (Hach NI-14 1416100, LaMotte 3110, LaMotte 3354)	Hach Spectrophotometer DR5000
Orthophosphate	Same as monitor (Hach PO-19 224800, Hanna HI 38061, Hanna HI 713)	Hach Spectrophotometer DR5000
pH	LaMotte Tracer 1749	Fisher Scientific accumet XL200
Total dissolved solids	LaMotte Tracer 1749	Fisher Scientific accumet XL200
Turbidity	LaMotte 7519	Hach Turbidimeter 2100P

B5.1.3 Replicates

ALLARM monitors will test each parameter twice (two replicates) and each value will be recorded onto their field data sheet. If the first two replicates fall within the acceptable range, the values will be averaged for the final result. If the values are not within the acceptable range, additional replicates will be tested until two values are within the acceptable range. Only those two values will be averaged for the final result. The other values will be crossed out by one line going through the middle of the number horizontally. The acceptable range for each parameter is based on the precision and sensitivity of the equipment used. Table B5-1 provides a summary of the parameters measured, testing order, equipment used, and the acceptable range.

Table B5-1. Summary of parameter testing order and acceptable range of field replicates for ALLARM monitors.

Testing Order	Parameter	Field/Home	Equipment	Acceptable Precision Range
1	Water temperature	Field	LaMotte armored Thermometer	± 1° C
1	Water temperature	Field	Hanna digital thermometer	± 0.5° C
1	Water temperature	Field	LaMotte DO meter w/thermometer	± 0.5° C
2	Water clarity	Field	Transparency tube	TBD
2	Water clarity	Field	Secchi disk	± 20 cm
3	pH	Field	Meter(s) (models TBD)	± 0.5 pH unit
3	pH	Field	Colorimetric kits (models TBD)	± 1 pH unit
3	pH	Field	ColorpHast pH Strips	± 1 pH unit
4	Conductivity	Field/Home	LaMotte Tracer PockeTester	± 10% or 10 μS/cm, whichever is greater
5	Total dissolved solids	Field/Home	LaMotte Tracer PockeTester	± 10 mg/L
6	Dissolved oxygen	Field/Home	LaMotte DO kit	± 0.6 mg/L

6	Dissolved oxygen	Field/Home	LaMotte DO meter	± 0.5 mg/L
7	Nitrate-nitrogen	Home	Hach nitrate kit	0 – 1 mg/L: ± 0.1 mg/L 1 – 10 mg/L: ± 1 mg/L
7	Nitrate-nitrogen	Home	LaMotte nitrate kits	Within 1 sensitivity unit of colorimetric scale
7	Nitrate-nitrogen	Home	Colorimeter; Spectrophotometer	0 – 1 mg/L: ± 0.1 mg/L 1 – 10 mg/L: ± 0.5 mg/L
8	Orthophosphate	Home	Hach orthophosphate kit	± 0.04 mg/L
8	Orthophosphate	Home	Hanna orthophosphate kit	± 0.04 mg/L
8	Orthophosphate	Home	Hanna digital orthophosphate checker	± 0.04 mg/L
8	Orthophosphate	Home	Colorimeter; Spectrophotometer	± 0.04 mg/L
9	Alkalinity	Home	LaMotte alkalinity kits	± 8 mg/L
9	Alkalinity	Home	Hanna digital alkalinity checker	± 5 mg/L
10	Turbidity	Home	LaMotte turbidity kit	± 5 JTU

B5.2.1 Analysis of Duplicate Samples by ALLARM Laboratory

The first time a monitor visits their site, they will collect a duplicate sample to send to the ALLARM Lab for analysis. At the lab, the sample will be tested for the same parameters the monitor measured (except for water temperature, water clarity, and dissolved oxygen), using the same brand and model equipment as the monitor. In addition, the ALLARM lab will test the samples using at least one alternative piece of equipment to document comparability between methods. The monitor's results will be compared to the results obtained by the ALLARM lab. In

order to “pass” the QC check, the results must be within a 20% relative percent difference (RPD) of each other, or the monitor’s results must fall within the acceptable precision range of the individual piece of equipment. The latter is used most often with values that are very low. Monitors will send in samples to the ALLARM Lab or participate in a Certification Workshop annually.

B6.1 Cleaning Requirements for ALLARM Monitors

ALLARM monitors are required to clean their monitoring equipment after each use, since used glassware can affect the monitoring results significantly. A summary of the cleaning procedures used for each parameter are included in Table B6-1, and the complete procedures are listed in the CMC Non-Tidal Methods Manual (Appendix C).

Table B6-1. Summary of equipment cleaning and maintenance requirements for ALLARM monitors.

Parameter	Equipment	Cleaning Methods Between Use
Water temperature	Thermometer	Rinse w/DI water
pH	ColorpHast pH Strips	Rinse vial w/DI water
Water clarity	Transparency tube	Rinse tubes w/DI water
Conductivity	LaMotte Tracer PockeTester	Rinse vial w/DI water
Total dissolved solids	LaMotte Tracer PockeTester	Rinse vial w/DI water
Dissolved oxygen	LaMotte DO Kit	5% Alconox soap, 10% HCl, rinse w/DI water
Nitrate-nitrogen	Hach Nitrate Kit	5% Alconox soap, 10% HCl, rinse w/DI water
Orthophosphate	Hach Orthophosphate Kit	5% Alconox soap, 10% HCl, rinse w/DI water
Alkalinity	LaMotte Alkalinity Kit	5% Alconox soap, 10% HCl, rinse w/DI water
Turbidity	LaMotte Turbidity Kit	5% Alconox soap, 10% HCl, rinse w/DI water