

Section 2: Chemical Monitoring

Chapter 4: Dissolved Oxygen

Chapter 5: pH

Chapter 6: Nutrients



Photos by Betsy Briggs at Lake Anna Photography and Alliance for the Chesapeake Bay

Chapter 4

Dissolved Oxygen

What is Dissolved Oxygen?

Oxygen found in aquatic systems is dissolved in water. This dissolved oxygen (DO) enters the systems from the atmosphere and from photosynthesis of aquatic plants (Figure 4-1). Currents and waves help introduce oxygen into the aquatic system due to more water being in contact with the atmosphere and better mixing of surface and deeper waters.

Why Monitor Oxygen?

Dissolved oxygen is one of the most important measures of water quality. An aquatic system with low levels of oxygen cannot support healthy populations of animal or plant life. If more oxygen is being used than is being introduced, organisms may weaken, move away, or die. Aquatic animals and plants use oxygen for respiration. Oxygen is also removed from the aquatic system through decomposition of organic material. Excessive nutrient levels from runoff, failing septic systems, or wastewater treatment plants can contribute to low dissolved oxygen levels by causing abundant growths of phytoplankton (microscopic plants and algae) called blooms. Living phytoplankton may deplete oxygen levels during the night and as the phytoplankton die, decomposition of the organic material by bacteria consumes oxygen.

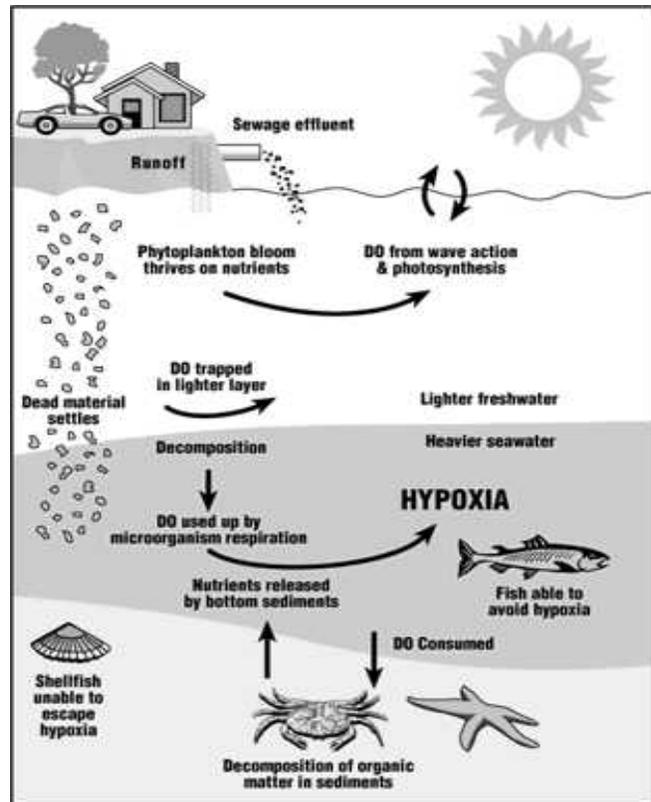


Figure 4-1. Processes affecting dissolved oxygen levels (from *Volunteer Estuary Monitoring: A Methods Manual, Second Edition*).

What Do Your Dissolved Oxygen Results Mean?

Dissolved oxygen (DO) is measured in mg/l (which is equivalent to parts per million or ppm). Aquatic organisms need a certain amount of dissolved oxygen in order to survive. The effects of low dissolved oxygen concentrations on aquatic organisms can be found in Table 4-1. Table 4-2 summarizes the water quality standards for dissolved oxygen in Virginia.

Table 4-1. Effects of Dissolved Oxygen on Aquatic Life

Levels of Dissolved Oxygen			
> 5 mg/l	Between 3 – 5 mg/l	<3 mg/l – Hypoxia Occurs (low dissolved oxygen levels)	<0.5 mg/l - Anoxia Occurs (lack of dissolved oxygen)
Level needed to support most aquatic life.	Aquatic organisms may become stressed.	Mobile organisms will move to areas of higher dissolved oxygen and immobile species may die.	Waters cannot support most aquatic life.

Table 4-2. Virginia Water Quality Standards for Dissolved Oxygen

	Most Waters	Stockable Trout Waters	Natural Trout Waters
Concentration of Dissolved Oxygen	Minimum 4 mg/l	Minimum 5 mg/l	Minimum 6 mg/l

Dissolved oxygen concentrations are affected by a number of variables such as time of day, depth, temperature, and salinity. Typically, DO concentrations of surface samples are highest around mid-day due to photosynthetic activity of aquatic plants. During the night, DO concentrations decline as DO is consumed through respiration while photosynthesis is halted due to the lack of sunlight. Therefore, DO levels are typically lowest in the early morning. Salt water cannot hold as much DO as fresh water (Figure 4-1). Lower DO concentrations are expected during the summer, since warm water cannot hold as much DO as cold water.

DO levels in lakes and estuaries can vary greatly with depth. During the summer months, vertical stratification (where warmer water is above colder water), can keep dissolved oxygen from reaching deeper waters. The deeper waters may maintain a low DO level until mixing occurs during storms or change of seasons.

The potential DO level, or DO saturation, is the maximum dissolved oxygen level possible under factors, such as temperature and salinity, which affect DO. Appendix 16 summarizes DO saturation levels at varying altitudes and water temperatures. Percent saturation is the amount of oxygen in the water relative to the potential DO level. Percent saturation can be determined as follows:

$$\% \text{ DO Saturation} = \frac{\text{Measured DO (mg/l)}}{\text{Saturated DO (mg/l) (from table 1 in Appendix 16)}} \times 100$$

Sample collection and test methods

Chapter 1 outlined a number of factors that every volunteer water quality monitoring program should consider. In addition to those summarized in Chapter 1, further considerations specific to monitoring for dissolved oxygen are discussed below.

When to Sample

Since DO fluctuates seasonally, it is best to sample DO throughout the year to obtain a more complete picture of water quality. If this is not possible, then sampling early spring through late fall may be preferred since critical DO levels are most common during warmer periods of the year. Since dissolved oxygen may fluctuate throughout the day, you may wish to sample about the same time of day so that your data does not show these fluctuations. This may be of particular interest if you are monitoring estuarine or lake waters and plan to track trends in DO levels.

Where to Sample

As described earlier, vertical stratification can affect DO levels at different depths. Since dissolved oxygen levels vary depending upon the depth, especially in the warmer months, volunteer monitoring programs may decide to measure DO at varying depths. This may be of particular interest if you are planning to monitor lakes or estuarine waters. Several water samplers designed to collect samples at different depths are shown in Figure 4-2. Meters attached to long cables can be used to collect profile data directly.

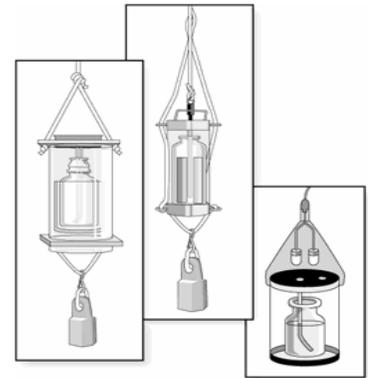


Figure 4-2. Dissolved oxygen samplers (from *Volunteer Estuary Monitoring: A Methods Manual, Second Edition*).

Choosing a Method

Dissolved oxygen can be easily and accurately measured using field test kits or meters. If using a meter, DO must be measured in the field. Some field test kits also require DO to be measured in the field, while others that are based on the Winkler titration method allow you to fix the water sample immediately upon collection and complete the analysis in a more desirable location within a few hours. The fixed samples must be stored in the dark without extreme temperature fluctuations.

Test Kits

Test kits may be more cost-effective than meters, but they do require replacement reagents once reagents expire or are used. Reagents also require proper storage, safety precautions, and proper disposal of waste. Monitors must follow protocols closely to ensure accurate results.

Titration methods with detection limits greater than 0.2 mg/l or those not based upon a Winkler method have limited uses, such as for educational purposes or to screen for potential problems. Winkler method titrations that measure DO in increments of 0.2 mg/l or less are acceptable for Department of Environmental Quality (DEQ) water quality assessments if the Quality Assurance Project Plan (QAPP) is approved by DEQ.

Recommended quality assurance/quality control (QA/QC) measures include collecting and testing two water samples simultaneously to verify that the sampling is being done correctly. The difference between the two samples should be no more than ± 0.6 mg/l. Because titrants are low concentration solutions that can lose strength over time and need to be replaced before their expiration dates (see Appendix 15 for list of commonly used test kit reagents). To ensure accuracy, it is recommended to verify titrants by checking against a standard before going out to the field to sample.



Volunteer measuring dissolved oxygen using a test kit (photo courtesy of Alliance for the Chesapeake Bay).

Located at the end of this chapter are instructions developed by the Alliance for the Chesapeake Bay when using the modified Winkler titration method.

Electronic Meters

While meters are more expensive than test kits, they offer the benefits of providing accurate results, and may allow the measurement of several parameters with one instrument. Data collected with meters are acceptable for DEQ water quality assessments if the protocols and QAPP are approved by DEQ.

A meter must be calibrated at the beginning of each sampling day. The calibration results should be acceptable when compared to the chart provided in Appendix 16. If the calibrated value is not within ± 0.2 mg/l of the chart, the meter should not be used and maintenance is required.

Additionally, the calibration should be confirmed at the end of the sampling day (this is referred to as a “post check”) to determine if the meter has drifted during the sampling day. The post check follows the methods of calibration without pressing the calibration button. The obtained meter value should be compared to the chart provided in Appendix 16. The meter reading should be within ± 0.5 mg/l of the table value. If the difference is not within this range, the data collected with the meter should be flagged. All calibration, post check, and QA/QC data should be recorded and kept on file.

Located at the end of this chapter are instructions and a sample calibration log sheet developed by DEQ for using dissolved oxygen probes.

Summary of Dissolved Oxygen Monitoring Methods

Method (Vendor and Catalogue #)	Approximate Cost	Monitoring Level (see Appendix 9)
Winkler Titration Test Kit (Hach #1469-00)	\$47.75 (100 tests)	I
Winkler Titration Test Kit (LaMotte #7414 [acid powder] or #5860 [liquid acid])	\$45.95 (50 tests)	I, II, or III
Meters (a multi-probe meter is more cost-effective than a single probe meter)	\$400-\$1000 (DO only) ~\$ 7500 (multi-parameter)	I, II, or III

Dissolved Oxygen: Modified Winkler Titration Test Kit- Protocols provided by the Alliance for the Chesapeake Bay

Equipment: LaMotte Dissolved Oxygen Test Kit 5860

Sodium Thiosulfate Check: (For Level III Quality Assurance)

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.

1. Rinse the titrating tube (small glass vial with plastic lid with hole in it) with a small amount of 10 mg/L Dissolved Oxygen Standard Solution. (Solution is available from HACH at www.HACH.com: Part number 40149)
2. Pour rinse into waste container.
3. Pour 20 ml of the Dissolved Oxygen Standard Solution into the rinsed titrating tube.
4. 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.
5. Fill titrating syringe to the “0” mark with Sodium Thiosulfate.
6. Titrate using the Sodium Thiosulfate.
7. When solution turns a pale yellow color, but not clear:
 - Remove cap, leaving syringe in cap.
 - 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.
8. Continue adding Sodium Thiosulfate until solution turns from blue to clear.
9. Read results on syringe - Record your results under the Dissolved Oxygen QA check on your field datasheet.
10. 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”.
11. Dispose of solution in titrating tube and syringe by pouring down sink and flushing with additional tap water.

Dissolved Oxygen- Modified Winkler Titration Field Collection

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 mg/L different than the first test, perform 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 sample water. If using a bucket do not return the rinse water to the bucket.

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 on the ground 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.

Titration

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. Slowly add the Sodium Thiosulfate to test tube and gently swirl the glass tube to mix. Continue this process until the yellow-brown solution in the glass tube turns a pale yellow or straw color. 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 8), 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 mg/L, 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 milligrams per liter (mg/l) of dissolved oxygen in the water sample.
12. Carry out Steps 6-11 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 mg/L, perform a third test and record the two results which are within 0.6 mg/L.

Calibrating Dissolved Oxygen Probes and Meters- Provided by the Virginia Department of Environmental Quality

Equipment: Various models of dissolved oxygen probes and meters

The instructions below are to be used with the DEQ supplied calibration log sheet to calibrate dissolved oxygen (DO) meters. With practice and proper care for the DO probe, users can complete the entire DO probe calibration process within 5-10 minutes.

Please 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).

Date- Record the date of calibration. Calibration must be done each day you collect DO samples

Temp C Pre Cal- Temperature of the probe just before you calibrate the probe

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 16 explains how to calculate the correct reading.

DO Theoretical 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 16.

Probe DO Level After Cal- 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.

After calibration, you may turn off the probe if the manufacturer says so. If not, please keep the probe on at all times while you are taking it out to the field and performing your field samples.

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.

Temp C Post Check- After you have placed the probe in the calibration chamber to equalize. 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. .

Barometric Pressure Post Check- 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 16.

Theoretical DO Level Post Check- As in the morning calibration, use Appendix 16 to determine your theoretical DO level.

DO Level Post Check- Record the 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.

Post Check Difference- 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. The color scale signifies the following:

Red- Displayed to show 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.

Yellow- Displayed to show a calibration difference of 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.

Green- Displayed to show if the calibration difference of 0.00 to 0.15 mg/L. The probe is functioning properly and no action is necessary except for general housekeeping according to manufacturer directions.

Initial- Please initial the person calibrating and using the probe for your records. This is good to know incase something happens to the probe while someone else was using it.

Notes- Space provided for any notes or comments regarding the probe.

Chapter 5

pH

What is pH?

pH is a term used to indicate the acidity or alkalinity of a solution as ranked on a scale from 0 to 14. Acidity increases as the pH decreases. The pH scale measures the concentration of hydrogen (H^+) and hydroxide (OH^-) ions, which make up water ($H^+ + OH^- = H_2O$). When both types of ions are in equal concentration, the pH is 7.0 or neutral. Below 7.0, the water is acidic (there are more hydrogen ions than hydroxide ions). When the pH is above 7.0, the water is alkaline, or basic (there are more hydroxide ions than hydrogen ions).

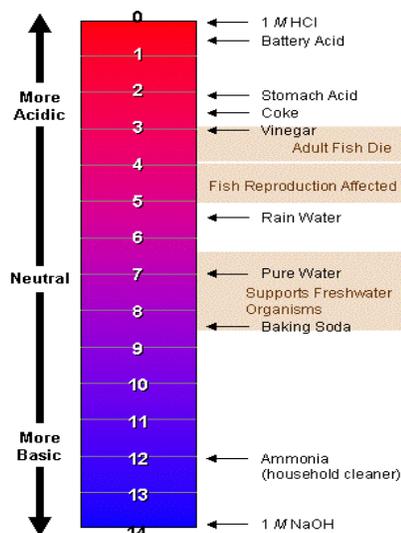


Figure 5-1. pH scale- (image from Virginia Cooperative Extension)

Why Monitor pH?

pH affects many chemical and biological processes in the water. For example, different organisms flourish within different ranges of pH. Most aquatic organisms prefer a pH range between 6.5 and 8. A pH value outside this range reduces the diversity in the waterway because it stresses the physiological systems of most organisms and can reduce reproduction. Low pH can also allow toxic elements and compounds to dissolve and become more "available" for uptake by aquatic plants and animals. This can produce conditions that are toxic to aquatic life, particularly to sensitive species like rainbow trout. Changes in acidity can be caused by atmospheric deposition (including acid rain), weathering of surrounding rock, certain wastewater discharges, and the decomposition of plants and animals.

What Do Your pH Results Mean?

The water quality standard in Virginia defines acceptable pH as being between 6 and 9. pH values above or below this range indicate a violation of our state's water quality standards.

Since the pH scale is logarithmic, a drop in the pH by 1.0 unit is equivalent to a 10-fold increase in acidity. For example, a water sample with a pH of 5.0 is 10 times more acidic than one with a pH of 6.0, and a pH of 4.0 is 100 times more acidic than a pH of 6.0. Changes in pH of just one or two units can be very stressful to aquatic organisms.

Sample collection and test methods

Chapter 1 outlined a number of factors that every volunteer water quality monitoring program should consider. In addition to those summarized in Chapter 1, further considerations specific to monitoring for pH are discussed below.

When to Sample

Since pH fluctuates daily and seasonally, it is best to sample pH throughout the year to obtain a more complete picture of water quality. Because pH, like dissolved oxygen, may fluctuate throughout the day due to photosynthesis, you may wish to sample about the same time of day so as not to confuse daily fluctuations with pollution events. pH is increased by photosynthetic activity, which results in daily fluctuations, especially on sunny, warm days. This is of particular interest if you plan to track trends in pH levels.

Choosing a Method

pH is easily measured and must be measured in the field within 30 minutes (immediately is preferable) of collection of the water sample.

Test Kits

Test kits may be more cost-effective than meters, but they require replacement reagents once they expire or are used. Test kits also require proper storage, safety precautions, and proper disposal of waste. Monitors must follow protocols closely to ensure accurate results. pH test kits are cheap, safe and easy to use.

If you plan on using a field test kit with a limited pH range (known as “narrow range” kits), you should first determine the average pH for your stream in order to select the correct range for your test kit. You can determine the average pH of your stream by either testing the stream with a wide range test kit (typically measures pH values from about 3-10) or locating existing pH data.

Since many citizen monitoring programs in Virginia use the LaMotte pH (liquid) test kits, the Department of Environmental Quality (DEQ) conducted a comparison study between these test kits and a reliable meter. These test kits were found to be useful in making general observations on water quality by DEQ if the Quality Assurance Project Plan (QAPP) is approved by DEQ. However, data from pH test kits are insufficient for DEQ to make water quality assessments because the color determinations may have a degree of subjectivity.



Volunteer measuring pH using a LaMotte test kit (photo courtesy of Alliance for the Chesapeake Bay).

Located at the end of this chapter are procedures developed by the Alliance for the Chesapeake Bay for using LaMotte pH test kits.

Electrometric Meters

While meters are more expensive than test kits, they can provide accurate and reliable results and may allow the measurement of several parameters with one instrument. Data collected with meters are acceptable for use by DEQ for water quality assessments if the protocols and QAPP are approved by DEQ.

A meter must have the ability to calibrate at least 2 well-separated pH values to meet DEQ's QA/QC requirements. A pH meter should be calibrated with at least 2 standard pH buffers (solutions of known pH values) for the range that are close to the expected sample pH values. If the pH value is usually below 7, then calibration should use the standard pH buffers 4.00 and 7.00. If pH value is usually above 7, then calibration should use buffers 7.00 and 10.00. Meters must be calibrated at the beginning of the day before samples are collected.

A post check must be conducted at the end of the day to determine if the meter has drifted during the sampling day. A post check means that you take pH readings for the same buffers you used at the beginning of the sampling day (this is not a calibration). The results for each buffer must be within ± 0.2 units of the buffer value. If the results are not within this range, the data collected with that meter should be flagged and maintenance or replacement of the probe is required. All calibration, post check and QA/QC data should be recorded and kept on file.

Located at the end of this chapter are instructions and a sample calibration log sheet developed by DEQ for using pH probes.

Summary of pH Monitoring Methods

Method (Vendor and Catalogue #)	Approximate Cost	Monitoring Level (see Appendix 9)
Wide Range (3.0 – 10.0) Field Test Kit (LaMotte # 2117)	\$33.00 (50 tests)	I or II
Various narrow range field test kits (LaMotte #2109, 2110, 2111, 2112) Use appropriate range	\$33.00 (50 tests)	I or II
pH Tester (Oakton Testr 2) *Must use standard buffers for calibration *Testr 2 meets DEQ's QA/QC requirements while Testr 1 does <u>not</u> .	\$75.00	I, II, or III
Meters (a multiprobe meter is more cost-effective than a single probe meter) *Must use standard buffers for calibration	\$200-\$1000 (pH only) ~ \$7500 multi-probe)	I, II, or III

pH Test Kit- *Protocols provided by the Alliance for the Chesapeake Bay*

Equipment: LaMotte pH kits (2109, 2110, 2111, 2112, 2117)

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 bucket.
2. Fill the sample test tube to the black line with water from the 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.

Calibrating pH Probes and Meters- *Provided by the Virginia Department of Environmental Quality*

Equipment: Various models of pH probes and meters

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 and reflects the pH found in the majority of Virginia waterways. 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.

Date- Record the date of calibration. Calibration must be done each day you perform samples.

Temp C Pre Cal- Temperature of the probe during calibration.

Pre Cal pH 7- 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.

Cal 7 Buffer- 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.

Pre Cal pH 4 (or 10)- Clean the probe with distilled or deionized water and blot dry and then immerse the probe in the 4.00 (or 10.00) buffer solution, record the stabilized value.

Cal 4 (or 10) Buffer- 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.

Temp C Post Check- Record the temperature of the probe at the end of the day when you are performing the calibration check.

pH 7 Post Check- Place the probe into the pH 7 buffer and ensure adequate mixing. Record the value the probe displays when it equalizes. **DO NOT** recalibrate the probe. The purpose of this end of day check is to detect unacceptable probe drift.

pH 4 (or 10) Post Check- Place the probe in the pH 4 (or 10) buffer and ensure adequate mixing. Again, record the value when it equalizes. **DO NOT** recalibrate the probe.

Difference for (7, 4 or 10) Buffer - These two columns calculate the differences based on the following color system:

Red- The pH difference is greater than 0.2 SU. Flag the data and repair/replace the probe.

Yellow- The pH is between 0.15 and 0.2 SU. The probe may need servicing soon.

Green- The pH difference is between 0.00 and 0.15 SU. The probe is functioning properly and no further action is necessary. Follow general housekeeping as outlined by the manufacturer.

Initial- Please initial the person calibrating and using the probe for your records.

Notes- Space provided for any notes or comments regarding the probe.

Chapter 6

Nutrients

What Are Nutrients?

Nutrients are necessary for the survival and growth of aquatic plants, which are the base of the food chain for all other aquatic organisms. Plants and algae need a number of nutrients (such as nitrogen, phosphorus, silica, carbon, potassium, calcium, and magnesium) for growth and reproduction. Of these nutrients, the lack of nitrogen and phosphorus limit plant growth in most aquatic system. For the purposes of this manual, we will refer to nitrogen and phosphorus when we speak about *nutrients*. The different forms of nitrogen and phosphorus will be discussed in further detail later in this chapter in the section entitled sample collection and test methods

Why Monitor Nutrients?

Nutrient levels in an aquatic system vary depending upon temperature, rainfall, runoff, biological activity, and the flushing of the aquatic system. Nutrient levels are generally higher in the spring and early summer and impact the aquatic system in several ways. High nutrient levels can accelerate eutrophication of a waterway. Eutrophication is characterized by abundant growths of phytoplankton (microscopic plants and algae) called algal blooms that may block sunlight from submerged aquatic vegetation (see Chapter 10). These algal blooms result in lower dissolved oxygen levels as decomposition of their organic matter consumes the dissolved oxygen.

Nutrient concentrations in aquatic systems are influenced by both natural and human sources. Natural sources of nitrogen and phosphorus include decomposition of organic matter, nitrogen fixation of atmospheric nitrogen by certain bacteria and algae, and geologic formations rich in nitrogen or phosphorus. Human sources include discharges from wastewater treatment plants, stormwater runoff, livestock wastes, fertilizer runoff from lawns and agricultural fields, groundwater seepage from failing septic systems, planting of nitrogen fixing plants (such as clover or beans) in agricultural fields, and atmospheric deposition (including acid rain) from the burning of fossil fuels.

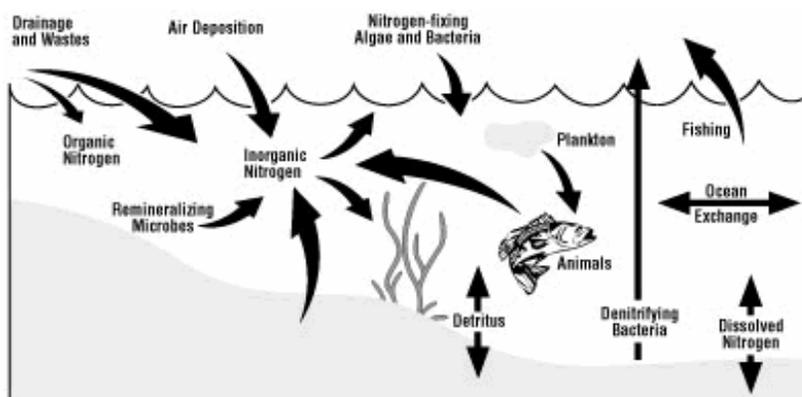


Figure 6-1. The nitrogen cycle (from *Volunteer Estuary Monitoring: A Methods Manual, Second Edition*).

What Do Your Nutrient Results Mean?

Developing nutrient criteria for the nation's waters is currently a hot issue. The debate centers on determining the limiting nutrient for a particular type of water in a particular ecoregion. Currently, Virginia has adopted water quality standards for some nutrients (such as total ammonia) as they relate to the toxicity to aquatic animals and nitrate for public drinking water supplies).

However other standards are still under development to establish criteria to various waterbody types and uses (e.g. lakes, streams and the Chesapeake Bay and its tributaries). Information on the criteria and development of these standards can be found on the following websites:

<http://www.chesapeakebay.net> and <http://www.deq.virginia.gov/wqs/>.

Sample collection and test methods

Chapter 1 outlined a number of factors that every volunteer water quality monitoring program should consider. In addition to those summarized in Chapter 1, several considerations specific to monitoring for nutrients are discussed below.

Different Forms of Nutrients

Nitrogen and phosphorus can be found in aquatic systems in many different forms, or species. While monitoring each individual species may help determine the source, it is important to remember that, when developed, Virginia's water quality standards may be for total nitrogen and total phosphorus.

Nitrogen Species

In aquatic systems, nitrogen exists in various inorganic chemical species (ammonia, nitrate and nitrite are all common components of synthetic fertilizers) and in particulate and dissolved organic and inorganic forms. Total nitrogen is a combination of nitrate, nitrite and Total Kjhedal Nitrogen (TKN). TKN is organic nitrogen, which is a complex mixture of compounds primarily derived from living and dead organisms.

Nitrification is the process whereby some bacteria convert ammonium to nitrite and then nitrite to nitrate. Since this process consumes oxygen, a system with low dissolved oxygen levels may experience decreased concentrations of ammonia and subsequently increased levels of nitrites. Nitrate is highly water-soluble and is easily carried by runoff. At high levels, nitrates and ammonia can be toxic. The natural level of ammonia and nitrate in discharge from wastewater treatment plants can be as high as 30 mg/l. However many of these facilities are now being required to lower the level of nutrients released into the environment.

Phosphorus Species

In aquatic systems, phosphorus exists as orthophosphate (dissolved and inorganic), total phosphorus (dissolved and particulate), organic phosphate, and polyphosphate (from detergents). Orthophosphate is commonly measured and is found in fertilizers. Phosphate that is not associated with organic material is inorganic and this inorganic phosphorus is the form required by plants. Animals can use either organic or inorganic phosphate. Many phosphorus species attach to soil particles and can be transported with sediment through runoff. Phosphate in the aquatic system may bind to minerals in the sediment resulting in low phosphorus levels in the water. During conditions of no dissolved oxygen, bound phosphorus can be released into the water column triggering algal blooms. Figure 6-2 shows the interaction of various forms of phosphorus in the environment.

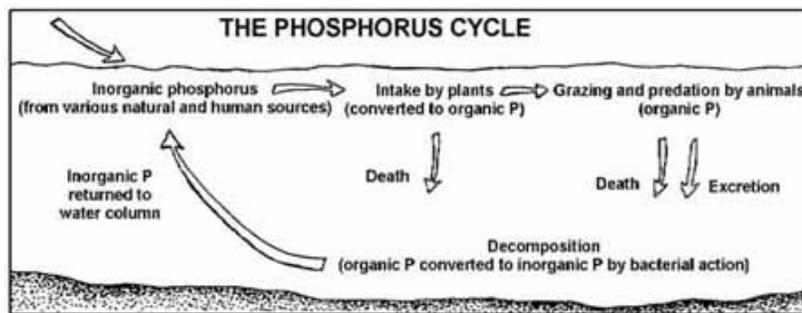


Figure 6-2. The phosphorus cycle (from *Volunteer Stream Monitoring: A Methods Manual, Second Edition*).

Monitoring phosphorus is challenging because it involves measuring very low concentrations (0.01 mg/l or even lower). Even such very low concentrations of phosphorus can have a dramatic impact on streams. Methods that do not have detection limits this low can be used to identify potential problem areas.

When to Sample

Since nutrient concentrations are highly variable, it is best to sample for nutrients throughout the year and over a long period of time to obtain a more complete picture of water quality. Frequent sampling can also facilitate explaining variability in the data.

Test Methods

Choosing a method for nutrient analysis can pose a dilemma. Your decisions on the goals of your program and the intended data use will determine the method that you should use. At this time, laboratory analyses of nutrients are the only methods that yield results accurate enough for DEQ's water quality assessments. Other methods may be used for educational or screening purposes.

Field Test Kits

Field test kits cannot measure total nutrient concentrations. Since water quality nutrient standards are written in terms of total nutrient concentrations (e.g. total nitrogen), information collected with test kits may only be used for screening purposes. Data collected from nutrient test kits are not acceptable for use by DEQ for water quality assessments. Different forms of nutrients can be measured using test kits to screen for potential problem areas or “hot spots”. In general, nutrients are found in low concentrations that may be lower than the detection limits of the test kits. However, test kits that detect low levels can collect information about periodic increases in nutrient concentrations and help target areas where more advanced monitoring may be of interest.

Laboratory Methods

There are various types of methods used by laboratories to measure nutrients. These methods depend on what type of nutrient species is being tested and equipment available to the laboratory. If a citizen volunteer group uses a laboratory for nutrient analysis, several recommend protocols need to be followed in order to DEQ to use the data in water quality assessment.

- Laboratory uses EPA approved or uses EPA recognized methods and the SOP used by the lab is approved by DEQ.
- Proper preservation of samples: Table 6-1 describes acceptable preservation methods of water samples for lab analysis of various nutrient species.
- Field splits: A field split is simply a second water sample taken at the same time as the first to measure the homogeneity of the samples. It is recommended that field splits are collected randomly for 10% of your samples (for a large sample size, 5% is acceptable). For example, if you collect 50 samples, you should collect 5 field split samples from random sites.
- Field equipment blanks are only necessary if water samples are collected in a bucket or other sampling device and transferred into the sample container. A field equipment blank uses pure and clean water (e.g. distilled or deionized water) rinsed through the sample collection devices to detect cross-contamination between sites. A field equipment blank is collected and transferred in the same manner as the stream water sample. It is recommended that you collect field equipment blanks randomly for 10% of your total samples (for a large sample size, 5% is acceptable).

Table 6-1. Preservation Methods for Laboratory Analysis of Various Nutrients

Parameter	Chill on Ice to <4°C (immediately)	Lower pH to < 2 (add 2 ml of sulfuric acid to 1 liter of sample)	Freeze (in the lab)	Holding Time
Total nitrogen	YES		YES	28 days
Ammonia/TKN	YES	YES		28 days
Nitrate/Nitrite	YES	YES		28 days
Total phosphorus	YES	YES		28 days
Orthophosphate	YES			48 hours

Summary of Nutrient Monitoring Methods

Method (Vendor and Catalogue #)	Approximate Cost	Monitoring Level (see Appendix 9)
Nitrate Test Kits (LaMotte #3119, 3519, 3615, 3354; HACH #14161-00)	\$53-\$83	I
Ammonia Test Kits (LaMotte #3304; HACH #2241-00, 24287-00)	\$55	I
Nitrite Test Kits [LaMotte #7674 (50 tests); HACH #21820-00 (100 tests)]	\$53-\$79	I
Phosphate Test Kits [LaMotte #3121, 7416, 3119 (50 tests); HACH #2248-00, 2248-01 (100 tests)]	\$65-\$87	I
Laboratory method	\$7.50- \$30.00 per sample per species*	I, II or III

*These costs are based upon submitting samples to the state laboratory, the Division of Consolidated Laboratory Services. This lab is only available to government organizations and nongovernmental organizations that receive state funding.