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Voluntary Estuary Monitoring Manual

Chapter 11: pH and Alkalinity

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Chapter 11

pH and Alkalinity



Every estuary is part of the carbon cycle. Carbon moves from the atmosphere into plant and animal tissue, and into water bodies. Alkalinity, acidity, carbon dioxide (CO_2), pH, total inorganic carbon, and hardness are all related and are part of the inorganic carbon complex. There are fascinating interrelationships among these factors. For example, the amount of carbon dioxide in the water affects (and is affected by) the pH and photosynthesis.

Photos (l to r): G. Carver, K. Register, R. Ohrel

Overview

This chapter discusses two additional chemical parameters of estuaries that are monitored to increase our understanding of the water's health: pH and alkalinity. Since the pH of water is critical to the survival of most aquatic plants and animals, monitoring pH values is an important part of nearly every water quality monitoring program. The testing is quick and easy and can establish a valuable baseline of information so that unanticipated water quality changes can be better understood.

Testing water samples for total alkalinity measures the capacity of the water to neutralize acids. This test is important in determining the estuary's ability to neutralize acidic pollution from rainfall or wastewater.

Every estuary is part of the carbon cycle. Carbon moves from the atmosphere into plant and animal tissue, and into water bodies. Alkalinity, acidity, carbon dioxide (CO_2), pH, total inorganic carbon, and hardness are all related and are part of the inorganic carbon complex. There are fascinating interrelationships among these factors. For example, the amount of carbon dioxide in the water affects (and is affected by) the pH and photosynthesis.

Why Monitor pH and Alkalinity?

Routine monitoring of a waterbody should provide baseline information about normal pH and alkalinity values. Unanticipated decreases in pH could be indications of acid rain, runoff from acidic soils, or contamination by agricultural chemicals. Values of pH outside the expected range of 5.0 to 10.0 should be considered as indications of industrial pollution or some cataclysmic event. Likewise, a long-term database on alkalinity values provides researchers with the ability to detect trends in the chemical makeup of estuary waters. ■

pH

pH is a measure of how acidic or basic (alkaline) a solution is. It measures the hydrogen ion (H^+) activity in a solution, and is expressed as a negative logarithm. The pH measurements are given on a scale of 0.0 to 14.0 (Figure 11-1). Pure water has a pH of 7.0 and is **neutral**; water measuring under 7.0 is **acidic**; and that above 7.0 is **alkaline** or **basic**. Most estuarine organisms prefer conditions with pH values ranging from about 6.5 to 8.5.

Values of pH are based on the logarithmic scale, meaning that for each 1.0 change of pH, acidity or alkalinity changes by a factor of ten; that is, a pH of 5.0 is ten times more acidic than 6.0 and 100 times more acidic than 7.0. When the hydrogen and hydroxyl ions are present in equal number (the neutral point), the pH of the solution is 7.

The Role of pH in the Estuarine Ecosystem

Water's pH is affected by the minerals dissolved in the water, aerosols and dust from the air, and human-made wastes as well as by plants and animals through photosynthesis and respiration. Human activities that cause significant, short-term fluctuations in pH or long-term acidification of a waterbody are exceedingly harmful. For instance, algal blooms that are often initiated by an overload of nutrients can cause pH to fluctuate dramatically over a few-hour period, greatly stressing local organisms. Acid precipitation in the upper freshwater reaches of an estuary can diminish the survival rate of eggs deposited there by spawning fish.

Several other factors also determine the pH of the water, including:

- bacterial activity;
- water turbulence;
- chemical constituents in runoff flowing into the waterbody;
- sewage overflows; and
- impacts from other human activities both in and outside the drainage basin (e.g., acid drainage from coal mines, accidental spills, and acid precipitation).

Estuarine pH levels generally average from 7.0 to 7.5 in the fresher sections, to between 8.0 and 8.6 in the more saline areas. The slightly alkaline pH of seawater is due to the natural buffering from carbonate and bicarbonate dissolved in the water.

The pH of water is critical to the survival of most aquatic plants and animals. Many species have trouble surviving if pH levels drop under 5.0 or rise above 9.0. Changes in pH can alter other aspects of the water's chemistry, usually to the detriment of native species. Even small shifts in the water's pH can affect the solubility of some metals such as iron and copper. Such changes can influence aquatic life indirectly; if the pH levels are lowered, toxic metals in the estuary's sediment can be resuspended in the water column. This can have impacts on many aquatic species. See Chapter 12 for more information on toxins. ■

Sampling Considerations

Chapter 6 summarized several factors that should be considered when determining monitoring sites, where to monitor, and when to monitor. In addition to the considerations in Chapter 6, a few additional ones specific to monitoring pH are presented here.

When to Sample

It is well-established that levels of pH fluctuate throughout the day and season, and a single pH measure during the day may not draw a very accurate picture of long-term pH conditions in the estuary. Photosynthesis by aquatic plants removes carbon dioxide from the water; this significantly increases pH. A pH reading taken at dawn in an area with many aquatic plants will be different from a reading taken six hours later when the plants are photosynthesizing. Likewise, in waters with plant life (including planktonic algae), an increase in pH can be expected during the growing season. For these reasons, it is important to monitor pH values at the same time of day if you wish to compare your data with previous readings. It is also important to monitor pH values over a long period of time to provide useful data. The actual time to measure pH will depend on local conditions and the monitoring goals of the volunteer program.

Choosing a Sampling Method

The pH test is one of the most common analyses done in volunteer estuary monitoring programs. In general, citizen programs use one of two methods to measure pH: (1) the colorimetric method or (2) electronic meters. Both require that measurements be taken in the field, since the pH of a water sample can change quickly due to biological and chemical processes.

Color comparator (also called "colorimetric") field kits are easy to use, inexpensive, and sufficiently accurate to satisfy the needs of most programs. The colorimetric method can also be used with an electronic colorimeter. If very precise measures are required, more expensive electronic pH meters provide extremely accurate readings. Test paper strips to obtain pH are *unsuitable* for use in estuarine waters since they do not provide consistent measurements in salt water. The following sections describe the use of the two common methods.

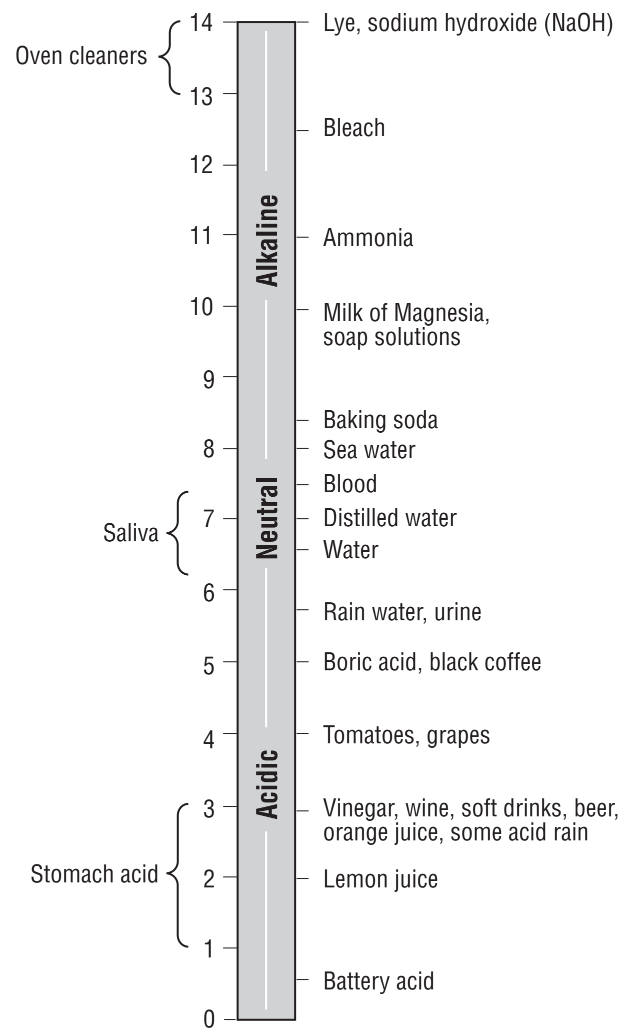

Figure 11-1. pH range scale.

Colorimetric Method

Colorimetric means "to measure color." In a colorimetric test method, reagents are added to a water sample, and a reaction occurs which produces a color. The color can be measured visually or electronically. This method is not suitable for water containing colored materials such as dissolved organic compounds or excessive algae. For water samples that are colored, a meter is suggested.

<u>Visual Method to Measure Color</u>

Field kits cover a range of pH values. They cost between $15 and $50, depending on the range of pH values to be tested. These kits come with several color standards built into a plastic housing unit or printed on a card. After adding reagents according to the instructions, the volunteer compares the color in the test tube with the standards to determine the pH value. If the general pH values of the estuary are known, pick a kit that includes these values within its range of sensitivity. Some programs prefer to use a wide-range kit that covers pH values from 3.0 to 10.0 until the measured range of values for that waterbody has been established. After determining the actual range over several seasons, switch to a narrower range kit for greater accuracy. Make sure kits have been checked against pH standards.

Electronic Method to Measure Color

An electronic colorimeter measures the amount of light that travels through the reacted sample and converts the measurement to an analog or digital reading (LaMotte, 1999). A reagent is added to the water sample in a test tube, which is then inserted into the colorimeter for analysis. Usually electronic colorimeters are capable of testing multiple water quality parameters.

pH Meters

Although more expensive than the colorimetric field kits, pH meters give extremely accurate readings of a wide range of pH values. The more economical pH testers cost about $40. Some more expensive meters ($75 - $750) also will display the water temperature, and some meters have cables so that you can obtain readings throughout the water column. Unlike the colorimetric method, meters can be used even if the water is clouded or colored. ■

Helpful Hint:
If your water quality monitoring program plans to collect data on alkalinity, pH meters with built-in temperature sensors are required rather than the colorimetric kits.

pH Calibration Standards

Whether you use a field kit, pH meter, or colorimeter unit, calibration standards (also called “buffer solutions”) are employed to ensure that your equipment is accurate. The standards most commonly used are pH 4.00 (or 4.01), pH 7.00, and pH 10.00. They are available in liquid or powder form (the powder is added to demineralized or deionized water). These pH standards cost from $5 to $25 each, depending on the quantity of calibrations you will be conducting.

Following is information regarding buffers:

- Because buffer pH values change with temperature, the buffer solutions should be at room temperature when you calibrate the meter. Usually you can calibrate your pH equipment at home, a few hours before using it. Check manufacturer’s instructions.
- Do not use a buffer after its expiration date.
- Always cap the buffers during storage to prevent contamination.
- Do not reuse buffer solutions!

How to Measure pH Values

General procedures for measuring pH are presented in this section for guidance only; they do not apply to all sampling methods. **Monitors should consult with the instructions that come with their sampling and analyzing instruments. Those who are interested in submitting data to water quality agencies should also consult with the agencies to determine acceptable equipment, methods, quality control measures, and data quality objectives (see Chapter 5)**.

Before proceeding to the monitoring site and collecting samples, volunteers should review the topics addressed in Chapter 7. It is critical to confirm the monitoring site, date, and time; have the necessary monitoring equipment and personal gear; and understand all safety considerations. Once at the monitoring site, volunteers should record general site observations, as discussed in Chapter 7.

Reminder!

To ensure consistently high quality data, appropriate quality control measures are necessary. See "Quality Control and Assessment" in Chapter 5 for details.

STEP 1: *Check equipment.*

In addition to the standard sampling equipment and apparel listed in Chapter 7, the volunteer should bring the following items to the site for each sampling session:

- pH colorimetric field kit; or
- pH meter with built-in temperature sensor; or
- colorimeter unit with reagents.

STEP 2: *Collect the sample.*

If you are using the colorimetric method to measure pH, you can fill the test tube by lowering it into the water. If using a meter, you can sometimes put the meter directly in the water—you don't need to collect a sample. But if monitoring from a dock or boat, you will need to collect a water sample using screw-cap bottles, Whirl-pak bags, or water samplers. Refer to Chapter 7 for details.

Volunteer using a color comparator, or colorimetric field kit (photo by K. Register).

STEP 3: *Measure pH values.*

Colorimetric Method

The colorimetric methods (both visual and electronic meter) use indicators that change color according to the pH of the solution. Follow the directions in your colorimetric kit.

Since the test tube for the colorimetric tests is small, a clean eyedropper is useful as you fill the tube with the correct amount of sample water. With colorimetric kits, you add a chemical or two (reagents) to your water sample, and compare the resulting color of the water sample to the color standards of known pH values. With the field kits, which use visual assessments, it is helpful to place white paper in the background of the tube to emphasize any color differences, especially if the sample's color is faint. Record the pH value of the standard that most closely matches the color of the sample. If the sample hue is between two standards, check your program's quality assurance project plan (QAPP) (see Chapter 5). Some QAPPs require you to average the values of the two closest standards, and record this number as the pH. Other plans require you to select the closest value, and do not allow you to average the values.

pH Meter

Consistent calibration of equipment will ensure that high quality data are collected. The pH meter should be calibrated prior to sample analysis and after every 25 samples according to the instructions in the meter manual. Use two pH standard buffer solutions (see the box, "pH Calibration Standards," page 11-4). After calibration, place the electrode into the water sample and record the pH. The glass electrode on these meters must be carefully rinsed with deionized water after each use to ensure accurate results in the future.

STEP 4: *Clean up and send off data.*

Volunteers should thoroughly clean all equipment.

Make sure that the data sheet is complete, legible, and accurate, and that it accounts for all samples. Volunteers should make a copy of the completed data sheet before sending it to the designated person or agency in case the original data sheet becomes lost. ■

TOTAL ALKALINITY

Alkalinity (also known as "buffer capacity") is a measure of the capacity of water to neutralize acids. Alkaline compounds such as bicarbonates, carbonates, and hydroxides, remove hydrogen ions and lower the acidity of the water (thereby increasing pH). They usually do this by combining with the hydrogen ions to make new compounds.

Alkalinity is influenced by rocks and soils, salts, certain plant activities, and certain industrial wastewater discharges. Some water can test on the acid side of the pH scale and still rank high in alkalinity! This means that, while the water might be acidic, it still has a capacity to buffer, or neutralize, acids.

Total alkalinity is measured by measuring the amount of acid (e.g., sulfuric acid) needed to bring the sample to a pH of 4.2. At this pH, all the alkaline compounds in the sample are "used up." The result is reported as milligrams per liter of calcium carbonate (mg/l $CaCO_3$).

The Role of Alkalinity in the Estuarine Ecosystem

Measuring alkalinity is important in determining the estuary's ability to neutralize acidic pollution from rainfall or wastewater. Without this acid-neutralizing capacity, any acid added to a body of water would cause an immediate change in pH. This buffering capacity of water, or its ability to resist pH change, is critical to aquatic life. The estuary's capacity to neutralize acids will vary between the freshwater reaches of the estuary and the portions with higher salinity.

Total Alkalinity Levels in Estuaries

Total alkalinity of seawater averages 116 mg/l and is greater than fresh water, which can have a total alkalinity of 30 to 90 mg/l, depending on the watershed. The brackish waters of an estuary will have total alkalinity between these values. ■

Sampling Considerations

Choosing a Sampling Method

For total alkalinity, a double endpoint titration using a pH meter and a digital titrator is recommended. This can be done in the field or in the lab. If you plan to analyze alkalinity in the field, it is recommended that you use a digital titrator. Another method for analyzing alkalinity uses a buret. For volunteer programs, using a digital titrator is recommended over the buret, because digital titrators are portable, economical, take less time, and have easy-to-read endpoints (results).

Digital Titrator

This method involves **titration,** the addition of small, precise quantities of sulfuric acid (the reagent) to the sample until the sample reaches a certain pH (the **endpoint**). The amount of acid used corresponds to the total alkalinity of the sample.

Digital titrators have counters that display numbers. A plunger is forced into a cartridge containing the reagent by turning a knob on the titrator. As the knob turns, the counter changes in proportion to the amount of reagent used. Alkalinity is then calculated based on the amount used. Digital titrators cost approximately $100; the reagents (chemicals) to conduct total alkalinity tests cost about $36. Additionally, alkalinity standards are needed for accuracy checks (see the box, "Alkalinity Calibration Standards," page 11-9). ■

Reminder!

To ensure consistently high quality data, appropriate quality control measures are necessary. See "Quality Control and Assessment" in Chapter 5 for details.

How to Measure Alkalinity

General procedures for measuring alkalinity are presented in this section for guidance only; they do not apply to all sampling methods. **Monitors should consult with the instructions that come with their sampling and analyzing instruments. Those who are interested in submitting data to water quality agencies should also consult with the agencies to determine acceptable equipment, methods, quality control measures, and data quality objectives (see Chapter 5).**

Before proceeding to the monitoring site and collecting samples, volunteers should review the topics addressed in Chapter 7. It is critical to confirm the monitoring site, date, and time; have the necessary monitoring equipment and personal gear; and understand all safety considerations. Once at the monitoring site, volunteers should record general site observations, as discussed in Chapter 7.

The alkalinity method described below (using a digital titrator) was developed by the Acid Rain Monitoring Project of the University of Massachusetts Water Resources Research Center (River Watch Network, 1992).

STEP 1: *Check equipment.*

In addition to the standard sampling equipment and apparel listed in Chapter 7, the volunteer should bring the following items to the site for each sampling session:

- digital titrator;
- 100-ml graduated cylinder;
- 250-ml beaker;
- pH meter with built-in temperature sensor;

- reagent (sulfuric acid titration cartridge, 0.16 N);
- standard alkalinity ampules, 0.500 N, for accuracy check; and
- bottle with deionized water to rinse pH meter electrode.

STEP 2: Collect the sample.

If you plan to analyze a water sample in the lab for alkalinity, then follow these collection and storage steps:

- Use 100 ml plastic or glass bottles.
- Label the bottle with site name, date, time, data collector, and analysis to be performed.
- Wearing gloves, plunge the bottle into the water. Fill the bottle completely and cap tightly.
- Avoid excessive agitation and prolonged exposure to air.
- Place the bottle in the cooler. Samples should be analyzed as soon as possible, but can be stored at least 24 hours by cooling to 4°C (39°F) or below. NOTE: Samples should be warmed to room temperature before analyzing (Hach, 1997).

STEP 3: Measure total alkalinity.

Alkalinity is usually measured using sulfuric acid with a digital titrator. Follow the steps below in the field or lab. Remember to wear latex or rubber gloves.

Add sulfuric acid to the water sample in measured amounts until the three main alkaline compounds (bicarbonate, carbonate, and hydroxide) are converted to carbonic acid. At pH 10, hydroxide (if present) reacts to form water. At pH 8.3, carbonate is converted to bicarbonate. At pH 4.5, all carbonate and bicarbonate are converted to carbonic acid. Below this pH, the water is unable to neutralize the sulfuric acid and there is a linear relationship between the amount of sulfuric acid added to the sample and the change in the pH of the sample. So, more sulfuric acid is added to the sample to reduce the pH by exactly 0.3 pH units (which corresponds to an exact doubling of the pH) to a pH of 4.2. However, the exact pH at which the conversion of these bases might have happened, or total alkalinity, is still unknown.

Arriving at total alkalinity requires an equation (given below) to extrapolate back to the amount of sulfuric acid that was added to actually convert all the bases to carbonic acid. A multiplier (0.1) then converts this to total alkalinity as mg/l of calcium carbonate ($CaCO_3$). To determine the alkalinity of your sample, follow these steps:

- Samples should be warmed to room temperature before analyzing.
- Insert a clean delivery tube into the 0.16N sulfuric acid titration cartridge and attach the cartridge to the titrator body.
- Hold the titrator, with the cartridge tip pointing up, over a sink or waste bottle. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to 0 and wipe the tip.
- Measure the pH of the sample using a pH meter. If it is less than 4.5, skip to step 3a, page 11-9.
- Insert the delivery tube into the beaker containing the sample. Turn the delivery knob while magnetically stirring the beaker until the pH meter reads 4.5. Record the number of digits used to achieve this pH. Do not reset the counter.
- Continue titrating to a pH of 4.2 and record the number of digits.
- Apply the following equation:

  Alkalinity (as mg/l $CaCO_3$) = (2a - b) x 0.1

  Where:

  a = digits of titrant to reach pH 4.5

  b = digits of titrant to reach pH 4.2 (including digits required to get to pH 4.5)

  0.1 = digit multiplier for a 0.16 titration cartridge and a 100 ml sample

Example:

Initial pH of sample is 6.5.

It takes 108 turns to get to a pH of 4.5.

It takes another 5 turns to get to pH 4.2, for a total of 113 turns.

Alkalinity = [(2 x 108) - 113] x 0.1
= 10.3 mg/l

- Record alkalinity as mg/l $CaCO_3$ on the data sheet.
- Rinse the beaker with distilled water before the next sample.

STEP 3a:

If the pH of your water sample, prior to titration, is less than 4.5, proceed as follows:

- Insert the delivery tube into the beaker containing the sample.
- Turn the delivery knob while swirling the beaker until the pH meter reads exactly 0.3 pH units less than the initial pH of the sample.
- Record the number of digits used to achieve this pH.
- Apply the equation as before, but a = 0 and b = the number of digits required to reduce the initial pH exactly 0.3 pH units.

Example:

Initial pH of sample is 4.3.

Titrate to a pH of 0.3 units less than the initial pH; in this case, 4.0.

It takes 10 digits to get to 4.0.

Enter this in the 4.2 column on the data sheet and note that the pH endpoint is 4.0.

Alkalinity = (0 - 10) x 0.1
= -1.0

- Record alkalinity as mg/l $CaCO_3$ on the data sheet.
- Rinse the beaker with distilled water before the next sample.

Note on Data Sheet for Alkalinity

Data sheets should be specialized depending on which methods your program uses to measure each parameter—and this is true for alkalinity, too. With the method described in this manual, your worksheet should include places for volunteers to record the results of the various steps described.

Alkalinity Calibration Standards

You will need to do an accuracy check on your alkalinity test equipment before the first field sample is titrated, again about halfway through the field samples, and at the final field sample. For this, you will need an alkalinity standard. Often, these come in pre-measured glass ampules. To use, break off the tip of the glass ampule and pour the liquid into a beaker. Then, follow the directions found under "Step 4: Perform an accuracy check." The price for the alkalinity standards is about $23 for 20 2-ml ampules.

STEP 4: Perform an accuracy check.

This accuracy check should be performed on the first field sample titrated, again about halfway through the field samples, and at the final field sample. Check the pH meter against pH 7.00 and 4.00 buffers after every 10 samples.

- Snap the neck off an alkalinity ampule standard, 0.500 N; or, if using a standard solution from a bottle, pour a few milliliters of the standard into a clean beaker.
- Pipet 0.1 ml of the standard to the titrated sample (see above). Resume titration back to the pH 4.2 endpoint. Record the number of digits needed.
- Repeat using two more additions of 0.1 ml of standard. Titrate to the pH 4.2 after each addition. Each 0.1 ml addition of standard should require 250 additional digits of 0.16 N titrant.

STEP 5: Return the field data sheets and/or samples to the lab.

Volunteers should thoroughly clean all equipment and transport the samples to the designated lab. Alkalinity samples must be analyzed within 24 hours of their collection. If the samples cannot be analyzed in the field, keep the samples on ice and take them to the lab or drop-off point as soon as possible.

Make sure that the data sheets are complete, legible, and accurate, and that they account for all samples. Volunteers should make a copy of the completed data sheets before sending them to the designated person or agency in case the original data sheet becomes lost. ■

References and Further Reading

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