Acid Buffering Capacity: Groundwater vs. Surface Water

Adapted from: An original Creek Connections activity. Creek Connections, Allegheny College, Meadville, Pennsylvania 16335.

Grade Level: intermediate, advanced

Duration: 45 minutes

Setting: lab or classroom

Summary: Students will study the alkalinity of several different water samples by determining how their pH levels are affected by acidic inputs.

Objectives: Students will understand what acid buffering capacity is and how it differs between types of water, while generating simple data sets and learning graphing and trend analysis skills.

Vocabulary: alkalinity, acid rain, acid mine drainage

Related Module Resources:
- pH Test #3 Activity
- HANBOOK: pH & Alkalinity sections
- FIELD MANUAL: p.33-35
- pH Information/Fact Sheet
- Alkalinity Info./Fact Sheet
- Rolaids Ingredients Sheet

Materials (Included in Module):
- seltzer (or other acid liquid)
- bottled spring water (limited amount)
- pH meters
- 1 mL eyedroppers measuring cup
- plastic cups
- materials containing calcium carbonate – Rolaids, antacids, (Opt.– see “Extensions”) Hach Alkalinity Kit (opt)
- geologic maps

Additional Materials (NOT Included in Module):
- Distilled water
- Additional bottled spring water
- other types of water samples
- crushed granite, glacial till

ACADEMIC STANDARDS (ENVIRONMENT AND ECOLOGY)

7th Grade:
4.1.7.B Understand the role of the watershed.
- Explain factors that affect water quality and flow through a watershed

4.3.7.B Describe how human actions affect the health of the environment.
- Explain how acid deposition can affect water, soil and air quality.

10th Grade
4.1.10.C Describe the physical characteristics of a stream and determine the types of organisms found in aquatic environments.
- Describe and explain the physical factors that affect a stream and the organisms living there

12th Grade
4.1.12. C Analyze the parameters of a watershed.
- Interpret physical, chemical and biological data as a means of assessing the environmental quality of a watershed

ACADEMIC STANDARDS (SCIENCE AND TECHNOLOGY)

7TH Grade
3.2.7.B Apply process knowledge to make and interpret observations.
- All subsections apply

3.2.7.C Identify and use the elements of scientific inquiry to solve problems.
- All subsections apply

10th Grade
3.2.10.B Apply process knowledge and organize scientific and technological phenomena in varied ways
- All subsections apply

3.2.10.C Apply the elements of scientific inquiry to solve problems
- All subsections apply

12th Grade
3.2.12.B Evaluate experimental information for appropriateness and adherence to relevant science processes.
- All subsections apply

3.2.12.C Apply the elements of scientific inquiry to solve multi-step problems
- All subsections apply

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BACKGROUND: (read other pH activities for more extensive background information).

Alkalinity, or acid buffering capacity, is a measure of the ability of a water system to resist changes in pH when acid is added to water. When a stream has high alkalinity, that stream is able to maintain a stable pH despite the addition of large amounts of acid. A stream that has a low alkalinity is poorly buffered and may undergo large, sudden drops in pH in response to acid inputs.

What causes this buffering affect? When there are carbonates (CO_3^{-2}) and bicarbonates (HCO_3^{-}) present in the water, they bond with the hydrogen (H^+) ions through a series of reactions. Hydrogen (H^+) ions bond with carbonate (CO_3^{-2}) that is dissolved in the water to form bicarbonate (HCO_3^-). The HCO_3^- ion then bonds with another H^+ ion from solution and forms carbonic acid (H_2CO_3). Carbonic acid can dissociate (break apart) into H_2O and carbon dioxide (CO_2), but it does not have to; it may react with other substances.

The equations for the above reactions follow:
1) $CO_3^{-2} + H^+$ --> HCO_3^-
2) $HCO_3^- + H^+$ --> H_2CO_3
3) H_2CO_3 --> $H_2O + CO_2$

How does carbonate and bicarbonate get added to the water? The answer lies in our region's geology. Sandstone, limestone, and dolomite contain the carbonates that, when dissolved in water, buffer against changes in stream pH. Sandstone and limestone are found in Western Pennsylvania. Carbonic acid also plays a role in the answer.

Carbonic acid (H_2CO_3) does not have to dissociate into water and carbon dioxide; instead it can react with carbonate based rocks such as sandstones, limestones, and dolomite as part of the rock's weathering process. Calcium carbonate ($CaCO_3$) makes up limestone and the cement that holds sandstone together, while magnesium carbonate ($MgCO_3$) makes up dolomite. Both can react with carbonic acid yielding either calcium bicarbonate $Ca(HCO_3^-)_2$ or magnesium bicarbonate $Mg(HCO_3^-)_2$ [$H_2CO_3 + CaCO_3$ ➢ $Ca(HCO_3^-)_2$]. The calcium (Ca^{+2}) and magnesium (Mg^{+2}) drop off as a solid to the stream bottom while 2 bicarbonates (HCO_3^-) remain, each able to react with one free hydrogen (thus maintaining the pH). This reaction yields carbonic acid again ($HCO_3^- + H^+$ H_2CO_3). That carbonic acid can start reacting with the calcium carbonate again to help buffer against even more hydrogen ions.

Watersheds with high alkalinity have the sandstones, limestones, and dolomites and the corresponding calcium carbonates/magnesium carbonates needed to help buffer a stream. Watersheds where the bedrock does not consist of sandstones and limestones, but instead have igneous rocks like granite and basalt, are unable to provide the needed calcium/magnesium carbonate that rid acidity. Streams in those areas have low alkalinity and can have low pH levels. An artificial source of alkalinity is lime (calcium carbonate), used to neutralize a stream. Lime is also used as a soil amendment to rid acidity in cropland, gardens, and lawns.

Groundwater has a higher alkalinity than creeks and streams. This is because the groundwater is in contact with the minerals, rocks, and soil and is able to dissolve the rocks and minerals. This gives the groundwater a higher amount of carbonate and bicarbonate dissolved in solution. Therefore, groundwater is better able to buffer against changes in pH.

Unlike groundwater, runoff from storms and snowmelt has a low amount of carbonate and bicarbonate, thus low alkalinity and possibly low pH. During the spring, heavy rains and melting snow can result in a large, sudden input of acid into hydrologic systems, too much to buffer, causing a rapid drop in pH. In some cases, such an “acid spike” results in fish kills as the pH drops below acceptable levels for supporting aquatic life.

Two major sources of acid into a stream are acid rain and acid mine drainage. **Acid rain** is caused by pollution emitted by factories and industry. Often the steam and smoke they release contains sulfuric acid (H_2SO_4) and nitric acid (HNO_3). When these cool in the atmosphere they are dissolved in the rainwater that falls to the ground and enters the streams as runoff. Sulfuric acid dissociates into two H^+ ions and one SO_4^{-2} ion and nitric acid breaks down into H^+ and NO_3^-. These additional hydrogen ions decrease the pH of the stream unless carbonate and bicarbonate are present in the stream to buffer against these changes.

Acid mine drainage is often the product of water running through abandoned mining operations from the early 1900s, and to a lesser extent active mining. Soil and crushed rock removed from above coal seams underground is called overburden and can contain iron pyrite (FeS_2, fool’s gold). The disturbance of this rock and soil exposes the pyrite to air and water, creating a chemical reaction forming ferrous iron (Fe^{+3}), iron hydroxide ($Fe(OH)_3$) and sulfuric acid (H_2SO_4). The acid can dissolve other minerals and metals from surrounding rock, and can itself dissociate (break apart) yielding sulfate (SO_4^{-2}) extra hydrogen ions (H^+) to the water (lowering the pH). So the acid mine drainage finds its way into groundwater and/or surface water, adding acidity (lowering the pH). Sometimes the pH level drops so low that the stream does not have enough alkalinity to buffer against the extra hydrogen ions.

The Environmental Protection Agency, EPA, suggests that a minimum of 20mg/L of calcium carbonate ($CaCO_3$) should be in a freshwater system so that it is able to support aquatic life.

OVERVIEW:

While recording pH levels, students will study the buffering ability of several different types of water. Acid (either seltzer or vinegar) will be added to water samples to determine which is most affected by the acid, changing the pH the most, and thus having the least buffering capacity. Graphs will be made of the data and comparisons of pH change and alkalinity will be made between samples.

PROCEDURE:

*Lemonade or Vinegar can be substituted for Seltzer for this experiment.

1. Prepare a rinse cup with distilled water or use distilled water wash bottles to clean off the pH meter between readings.

2. Pour 100 mL (0.1 L) of each water sample (groundwater, creek water, distilled water, rainwater, bottled spring water, tap water etc.) into appropriately labeled plastic cups. The amount must be the SAME in each cup.

3. Calibrate the pH meter using the instructions in Test Kit Instruction Section of the Module Resource Guide.

4. Pour seltzer into a labeled plastic cup. Take the pH of the seltzer using the instructions. The seltzer should be acidic. Enter this value on the appropriate line on the data sheet.

5. Rinse the pH meter, and then test the pH of each water sample (rinse between each sample). Record each in the appropriate data column at the initial level.

6. Using the eyedroppers (marked with a 0.5 and 1.0 mL line), add **0.5 mL** seltzer to each of the four water samples. Mix gently. Record the pH in the appropriate place on the data table.

7. Repeat step 5 until a total of 2.0 mL of seltzer has been added to each sample.

8. Let the sample with 2.0 mL of seltzer sit for 10 minutes and then measure the pH again. Record this value in the appropriate area on the data table. While the students are waiting they can continue on to step 9.

9. Use the blank graphs on the data sheet to plot some of your findings. Remember that you can plot a few samples on each graph to compare them (as long as you use a key to identify which one is which!). Have your teacher specify which samples you should graph.

DISCUSSION:

Discuss the results with the students. Did everyone get similar results? What do the results mean in terms of alkalinity? Which samples were acidic at the end of the activity? Basic? Neutral? (*1-6.9- acidic, 7-neutral, 7.1-14 basic)*

Why did the pH of all the samples go down (they most likely did)? Does that mean there was no alkalinity in the samples? *No, there was alkalinity, but it may have not had the reaction time needed to completely buffer the acidic additions. The addition of acid may have used up the available carbonate ions that buffered the solution against changes in pH. But what is important to look at in the results is which sample had the slowest decrease in pH. Alkalinity kept it from falling at a faster rate.*

Which solutions were the most resistant to changes in pH? (i.e. which had the highest acid buffering capacity?)*(probably groundwater, or bottled spring water –depending on where it is from)* Which were least resistant? *acid rain water* Why? *It depends on which kind of water had the most calcium carbonate in it, which is responsible for acid buffering capacity in this geographic area. Usually groundwater is rich in calcium carbonate. Usually rain does not contain alkalinity and is already acidic, so adding acid to acid just makes the solution more acidic.*

Which water would be most affected by acid rain? *The one that changed the most with the seltzer additions.* Least affected? *The one that changed the least from the seltzer additions.*

Why might the pH levels start to rise again if you let the samples sit for a while after the 2.0mL of acid (seltzer) are added? *The sample water has been given more reaction time to remove excess H+ ions, thus raising the pH. The chemical reaction of buffering is not always instantaneous.*

EVALUATION:

- Have the students choose two of the water samples tested and explain to the class how the alkalinity of the two samples was different and what may have caused this difference. (*i.e. groundwater may have had a lower change in pH than surface water because it is in contact with rocks, soil, and minerals which dissolve into the sample while surface water has no time to dissolve rocks, such as limestone which act as a buffer)*
- Analyze a data set by creating a graph.
- Discussion questions above.

EXTENSIONS AND MODIFICATIONS:

- Use different acid sources (seltzer, sprite, vinegar, acid mine drainage, etc.) and compare the results they yield.
- Compare different commercial acid buffers (Rolaids, AlkaSeltzer, Bufferin, etc.- provided in module) by adding ½ teaspoon of ground up tablet to similar water samples and repeating acidic additions.
- Compare different soil types (granitic, glacial till, etc. – not provided in module) by adding ½ teaspoon of ground soil to water and repeating readings.
- Compare different water sources (pond, lake, stream, spring, etc.)
- When the experiment has been completed, take some of the original sample waters and perform an alkalinity test on them. Compare these values with the data set generated. Are the results the same? *(Higher alkalinity levels should be seen in the samples that the seltzer had little effect on.)* Do the alkalinity test on the water samples after the seltzer has been added and see if a reduction in alkalinity levels is detectable.
- Do the alkalinity test on the water samples before the start of the experiment. Predict which water samples will be most affected by seltzer.

NOTES (TEACHERS, PLEASE WRITE ANY SUGGESTIONS YOU HAVE FOR TEACHERS USING THIS ACTIVITY IN THE FUTURE):

Activity Version: November 2021

DATA SHEET: Acid Buffering Capacity

Student Name___________________________________ Date______________

pH of seltzer_____________

pH values for experiment

Seltzer additions	Distilled Water	Surface Water	Ground water	Rain water	Other (if applicable):	Other (if applicable):
Initial pH						
0.5 mL seltzer						
1.0 mL seltzer						
1.5 mL seltzer						
2.0 mL seltzer						
2.0 mL seltzer after 10 min (do not graph)						

Graph two of your samples on the each of the axes below: