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Carolina™ Acid Deposition for AP Environmental Science

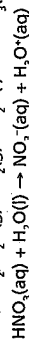
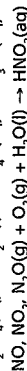
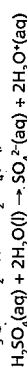
In this lab, you will measure the pH of unpolluted water and simulated acid rain and model the effects of acid rain on human-made structures. You will also determine the buffering effects of three types of bedrock (granite, basalt, and marble) and observe teacher demonstration tests of the pH and alkalinity of water samples collected locally to determine their sensitivity to acid deposition.

Background

Acid Deposition

Acid deposition consists of acidic (pH \leq 5.0) substances or acid-forming substances that fall to earth. These materials may be wet (e.g., rain, snow, and fog) or dry (e.g., particles of sulfate and nitrate salts).

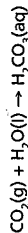
Despite significant reductions in air pollutant emissions, acid deposition remains a threat to human-made structures, aquatic organisms, forests, and, indirectly, human health. Acid deposition forms when gaseous sulfur dioxide and nitrogen oxides (nitrogen monoxide, nitrogen dioxide, and dinitrogen monoxide) are released into the atmosphere. These gases react with oxygen and water in the atmosphere to form sulfuric and nitric acids and sulfate and nitrate salts.



Many natural events, such as volcanic eruptions, forest fires, hot springs, and natural geysers, produce sulfur dioxide and nitrogen oxide gases. Human activity makes a significant contribution. In fact, anthropogenic (human-made) input of sulfur into the atmosphere almost equals that from natural events. For nitrogen oxides, anthropogenic input does equal that from natural events. The major sources of anthropogenic sulfur dioxide are coal-burning electric utilities and industrial plants. The major sources of anthropogenic nitrogen oxides are coal-burning electric utilities and motor vehicles.

The Hydrologic Cycle

As precipitation falls, carbon dioxide present in the atmosphere dissolves in the water and reacts to form carbonic acid, H_2CO_3 , a weak acid. For this reason, unpolluted rainwater is acidic, with a pH value around 5.6.



When precipitation reaches the ground, it runs off into surface water (streams and lakes) or infiltrates the soil. The water that infiltrates the soil percolates through permeable rock and into groundwater. Both surface water and groundwater proceed toward the ocean. Water returns to the atmosphere when surface water evaporates and plants transpire.

Areas Affected by Acid Deposition

The major sources of sulfur dioxide emitted in the United States are coal-burning electric utilities (70%), whereas the major sources in Canada are industrial plants (60%). The gases rise into the atmosphere and are carried east and northeast by prevailing westerly winds. These winds can disperse the pollutants

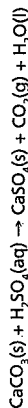
hundreds of miles from their source. In fact, most of the acid deposition that affects the northeastern U.S. and eastern Canada originates in the American Midwest. As these gases are carried by the winds, they react to form sulfuric and nitric acids as well as sulfate and nitrate particles. Acid deposition is a regional rather than global problem because of the limited force of the wind currents. Even so, winds carry air pollutants over political borders and create tension between neighboring countries. For example, tensions ran high in the late 1980s when it was found that air pollutants originating in the U.S. were being blown into Canada.

Major areas affected by acid deposition include the northeastern section of the United States and southeastern Canada. Acid deposition in these regions is intensified due to the large number of factories and coal-fired power plants in the Midwest. Areas of central Europe and Scandinavia also are affected by acid deposition due to directional winds carrying pollutants from British and other European factories. Large parts of Asia, including India and China, are affected by acid deposition due to their reliance on coal-fired plants for energy and industrial production.

Effects of Acid Deposition

Acid deposition affects plants, human-made structures, surface water, aquatic species, and human health. Acid deposition damages the leaves and bark of trees, impairing the plants' ability to photosynthesize and leaving them vulnerable to insects and disease. The acid removes the leaves' coating and burns them, leaving brown spots. Acid deposition leaches calcium and magnesium from the soil, depriving already weakened trees of essential minerals. The acid's reaction with soil minerals releases toxic aluminum ions that can damage plant roots. Trees at higher elevations are especially susceptible to acid damage, because cloud vapor can be 10 to 100 times more acidic than acid rain and can bathe trees in acid for days at a time. As water evaporates from the acidic droplets on a plant, their acidity increases. Acid deposition erodes some building materials and corrodes metals.

Many statues and buildings are made of calcium carbonate (CaCO_3) in the form of marble or limestone. Both marble and limestone react with acid deposition to form calcium sulfate, carbon dioxide, and water.



Calcium sulfate binds soot and dust. Buildings and sculptures affected by acid deposition turn black and must be cleaned in order to retain their intended appearance. In addition, calcium sulfate dissolves readily in water. If the affected object is exposed to wet acid deposition or even to pure water, it simply dissolves. The Parthenon, Taj Mahal, and Colosseum all show signs of erosion. It is estimated that 20% of this type of erosion is due to acid deposition.

Perhaps the best-known effect of acid deposition is the acidification of surface water and the resultant harm to aquatic species. As fish and amphibians develop, the eggs are particularly sensitive to changes in pH. Although tolerance varies by species, a pH of 5 or lower generally results in fish eggs' not hatching. Suboptimal pH is not necessarily lethal, but often leads to lower body weight and smaller size. The aluminum ions released from soil by acid deposition may enter lakes and stimulate excessive mucus formation in fish. This mucus clogs gills and asphyxiates many kinds of fish. A decline in pH-sensitive organisms disrupts an ecosystem and seriously affects its food web.

Acid deposition affects factors other than pH of the water. The influx of nitrogen from nitric acid deposition contributes to eutrophication. Symptoms of eutrophication include both toxic and nontoxic algal blooms, declines in the health of fish and shellfish, and a decrease in dissolved oxygen. Eutrophication brought about by anthropogenic sources such as acid rain can greatly alter the biodiversity of aquatic ecosystems.

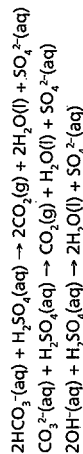
The U.S. Environmental Protection Agency conducted a National Surface Water Survey to identify lakes and streams suffering from chronic acidity and to determine the percentage of these waters that were chronically acidic due to acid deposition. The survey revealed that acid deposition is responsible

for approximately 75% of acidified lakes and 50% of acidified streams. The affected areas include the Adirondacks, mid-Appalachian highlands, upper Midwest, and high-elevation West. In the northeastern U.S., where there is poor buffering capacity, some lakes now have a pH lower than 5. Little Echo Pond in Franklin, New York, is one of the most acidic lakes reported, with a pH of 4.2.

Acid deposition does not cause direct harm to people; however, the pollutants that cause acid deposition directly affect human health. Lung cancer, asthma, bronchitis, and emphysema can be caused and aggravated by air pollutants. For example, cases of respiratory ailments are 50% higher in the most polluted parts of Poland, Hungary, and the Czech Republic than in cleaner areas of those countries. Senior citizens, children, and people with weakened immune systems are advised to stay inside during times of peak air pollution in many metropolitan cities.

How Is Acid Deposition Neutralized?

Surface waters and soils neutralize acid deposition in the same way they neutralize unpolluted precipitation. In aquatic studies, this property is referred to as *acid-neutralizing capacity (ANC)* or *alkalinity* and, in soil science, as *buffering capacity*. The major contributors to alkalinity in surface water are hydrogen carbonates (HCO_3^-), carbonates (CO_3^{2-}), and hydroxides (OH^-) that originate from minerals and rocks that the water encounters as it flows. Soils also affect ANC. Soils that have a large buffering capacity, such as those derived from limestone bedrock, provide lakes and streams with large ANC values. Soils with low buffering capacity, such as soils derived from inert bedrock (granite) and thin soils (common at high elevations), afford waterways with small ANC values. For example, approximately 500 of the streams in the mid-Atlantic coastal plains are acidic primarily due to acid deposition. This is partially because granite is the primary bedrock in those locations, allowing for little or no buffering of the acid precipitation that falls there. In the New Jersey Pine Barrens, over 90% of the streams are acidic, the highest proportion of acidified streams in the nation. More than 1,350 of the streams in the mid-Atlantic highlands are acidic, primarily due to acid deposition. These low pH levels are often too acidic to support aquatic animals such as trout, bass, salamanders, crayfish, snails, and mayflies. The environmental impact quickly rises to higher trophic levels. For example, the Common Loon relies on fish as its main food and seldom breeds on acidic lakes (pH < 5.5). Surface waters in the high-elevation West, such as the Cascades, Sierra Nevadas, and Rocky Mountains, also have low ANC. Ironically, the Midwest, where major air pollutants are located, is well equipped to neutralize acid deposition because its soils are derived from limestone bedrock and have a large buffering capacity. The following are some of the common neutralization reactions:



Alkalinity is measured in either $\mu\text{eq/L}$ or ppm CaCO_3 (see Notes 2, 3, and 4 at the end of this Background). In both units of measure, the greater the number, the greater the bedrock and soil's ability to neutralize the water's acidity. Use the following relation to interconvert ppm CaCO_3 and $\mu\text{eq/L}$.

$$X \text{ ppm } \text{CaCO}_3 = 20X \mu\text{eq/L}$$

Water with ANC $\leq 0 \mu\text{eq/L}$ is acidic by definition. Water with ANC $\leq 50 \mu\text{eq/L}$ may experience episodic acidification that results from snowmelt or heavy rainfall. Water with ANC $\leq 200 \mu\text{eq/L}$ is sensitive to acid deposition. For example, approximately 70% of sensitive lakes in the Adirondacks are at risk of episodic acidification. In the mid-Appalachians, approximately 30% of sensitive streams are likely to become acidic during an episode. Episodic acidification can cause fish kills and other ecological disruptions.

Solutions

Title IV of the Clean Air Act Amendments, enacted in 1990, regulates emissions of sulfur dioxide and nitrogen oxide compounds. The EPA established the Allowance Trading System in 1995. This program allocates permits called allowances to regulated companies. One allowance is for the emission of 1 ton of sulfur dioxide per year. A company's yearly allowances may be used in the year allocated or saved for future use. Companies can even buy, sell, or trade allowances. Nitrogen oxides are regulated with a rate-based regulatory system. This sets a limit on the pounds of nitrogen oxides per million British thermal units (lb/mmBtu) emitted by every power plant's stacks.

One method in which coal-fired power plants can reduce their emissions of sulfur dioxide is through burning coal that contains less sulfur. Low-sulfur coal is 0–1% sulfur, whereas high-sulfur coal is 2–4% sulfur. Sulfur dioxide emissions can be reduced through the installation of wet scrubbers. Though costly to install at existing power plants, scrubbers can remove 80–95% of emitted sulfur dioxides. Another method, fluidized bed combustion, creates an environment in which combustion occurs at a lower temperature and flue gases come into contact with sulfur-absorbing materials such as limestone that capture the sulfur oxides. The lower temperatures also reduce the formation of nitrogen oxides. This process reduces emissions of sulfur oxides by approximately 90% and nitrogen oxides by 15–35%.

Notes

1. Winds are often named for the direction from which they flow; for example, the prevailing westerlies blow from west to east.
2. One equivalent (eq) of a substance is the quantity in moles of that substance that neutralizes one mole of hydrogen ions, H^+ . For example, only one-half mole of CaCO_3 is required to neutralize one mole of $\text{CO}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{CO}_3(\text{aq})$. The calcium ion does not react with the hydrogen ion. One equivalent of calcium carbonate equals one-half mole of calcium carbonate.
3. Parts per million (ppm) refers to the number of parts of a substance per million parts of another substance. For example, 1.8 mg of calcium carbonate in 1.0×10^6 mg of water is 1.8 ppm. Because the density of water is 1.0 g/mL, the mass of 1 L of water is 1,000 g or 1.0×10^6 mg. Therefore, 1.8 ppm calcium carbonate is 1.8 mg calcium carbonate per liter of water.
4. The results of alkalinity tests are recorded as ppm CaCO_3 . Although water may contain chemicals other than calcium carbonate, the identity of these chemicals is unimportant; the test results are treated as if the water contained only calcium carbonate. In this way, the test results are standardized and may be compared directly and easily. Calcium carbonate serves as the reference because it is ubiquitous in natural waters.

Activity 1: Determining the pH of Unpolluted Rain**Materials**

- 2 glass test tubes
- straw
- pipet
- bromthymol blue
- tap water
- test tube rack
- graduated cylinder
- waste container for bromthymol blue waste

Procedure

1. Pipet 5 mL of tap water into the first test tube.
2. Add 1 drop of bromthymol blue, and determine if the pH of the water is acidic or basic. Bromthymol blue is blue at or above pH 7.6 and yellow at or below pH 6.
3. Record your observations in your lab notebook.
4. Pipet 5 mL of tap water into the second test tube. Exhale gently through a straw into the water for 30 seconds.
5. Add 1 drop of bromthymol blue, and determine whether the pH of the water is acidic or basic.
6. Record your observations in your lab notebook.
7. Dispose of the bromthymol blue waste in the designated waste container.
8. Rinse the test tubes with clean water, dry them, and return them to the Activity 1 materials station.

Activity 2: Modeling Acid Rain**Materials**

- glass test tube
- test tube rack
- ring stand with clamps (or test tube tongs)
- bromthymol blue
- match
- waste container for used matches

Procedure

1. Start with a dry test tube. If necessary, shake out any water in the test tube before proceeding.
2. Place 3 drops of bromthymol blue in the test tube.
3. Tilt and rotate the test tube so that the liquid coats the inner surface of the test tube.
4. Invert the test tube and clamp it to a ring stand. Alternatively, hold it with test tube tongs.
5. Determine whether the pH of the bromthymol blue drops indicates an acid or a base.

6. Record your observations in your lab notebook.
7. Light a match and immediately hold the flame beneath the inverted test tube, allowing the smoke to rise into the tube. Hold the match for a few seconds only, and immediately extinguish the flame if it has not gone out already.
8. Place used matches in the match disposal container.
9. Observe the liquid drops inside the tube. Determine whether the pH of the bromthymol blue indicates an acid or a base.
10. Record your observations in your lab notebook.
11. Rinse the test tube with water, dry it, and return it to the Activity 2 materials station.

Activity 3: Effects of Acid Rain on Human-Made Structures**Materials**

- half piece of chalk
- piece of mossy zinc
- mortar and pestle
- 50 mL of 0.05 M sulfuric acid labeled "Concentrated Acid Rain"
- 2 beakers
- graduated cylinder
- waste container

Procedure

1. Using a mortar and pestle, crush half of a piece of chalk into small pieces. The chalk should be crushed, not finely ground or powdered.
2. Place the chalk in a small beaker.
3. Place the mossy zinc in the other small beaker.
4. Using the graduated cylinder, measure and pour 25 mL of the Concentrated Acid Rain into each of the beakers.
5. Observe and compare the reactions of the samples for 5 minutes.
6. Record your observations in your lab notebook.
7. After 5 minutes, dispose of the sulfuric acid into the designated waste container and throw away any unused chalk.
8. Thoroughly rinse the mossy zinc and the small beakers, and return these materials to the Activity 3 materials station.

Activity 4: Effect of Soil and Bedrock on Acid Rain

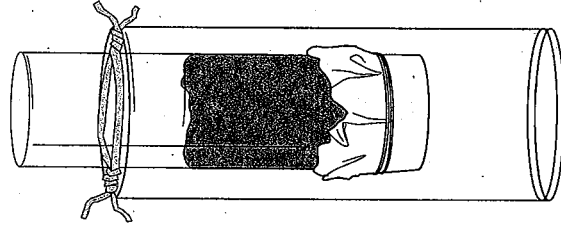
Materials

- 3 test tubes
- 3 columns
- 3 plastic vials
- test tube rack
- pH test strip vial
- cheesecloth (cut into 9 6-cm square pieces)
- scissors
- pipet
- 3 rubber bands
- 6 twist ties
- 8–10 small marble chips
- 8–10 basalt chips
- 8–10 granite chips
- clay sample
- sand sample
- humus sample
- 30 mL of "Acid Rain"
- metric ruler
- permanent marking pen
- small spoons or scoops

Procedure

Part 1: Soil

1. Prepare three different soil columns. You will place a different type of soil (clay, sand, or humus) in each.
 - a. Cut the cheesecloth into nine small pieces, each approximately 6 cm x 6 cm.
 - b. Cover the bottom of each column with three layers of cheesecloth. This will prevent the soil samples from falling out.
 - c. Use a rubber band to attach the cheesecloth securely to one end of each column, as shown in the illustration. Cut away any excess cheesecloth so you can clearly see the interior of the column.
 - d. Attach 2 twist ties about 3 cm from the top of each column; wrap and twist them as shown in the illustration.
 - e. Use a marker to label one tube "clay," one tube "sand," and one tube "humus."
 - f. Add 3 cm of the appropriate soil type into each labeled tube. Allow enough room for the "Acid Rain" to be poured in at the top of the column.



2. After all three columns are ready, use a twist tie to suspend each column in a different vial.
3. Pipet 5 mL of "Acid Rain" into each soil column.
4. Let the soil columns drain while you complete Part 2 of this activity.
5. When instructed, use a pH test strip to determine the pH of the drainage from each column.
6. In your lab notebook, record the pH of the drained "Acid Rain."
7. Dispose of the drainage (waste sulfuric acid) in the waste container provided.

Part 2: Bedrock

1. Label three test tubes with the names of three different types of bedrock, "marble," "basalt," and "granite," respectively.
2. Place 8 to 10 bedrock chips of the appropriate type into each labeled test tube.
3. Pipet 3 mL of "Acid Rain" into each test tube.
4. Gently mix the contents of each test tube by swirling each tube for 30 seconds.
5. Use a pH test strip to measure the pH of each solution.
6. In your lab notebook, record the pH of the "Acid Rain" after it was exposed to each type of bedrock.
7. Dispose of the contents (waste sulfuric acid) in the waste container provided.
8. Rinse the test tubes with clean water, dry them, and return them to the materials station.
9. Return to Part 1 to test the drainage from the clay, sand, and humus soil columns.

Laboratory Questions

1. In Activity 1, how did breathing into the tap water cause the solution to become acidic? What does exhaling into the water simulate from the environment? Write the chemical equation that explains the acidity of unpolluted rain.
2. In Activity 2, what gas does the burning match release? How does this simulate pollution that occurs in the environment? Why did the pH of the indicator solution change as the match burned? Write the chemical equations (3) that describe how this gas produces wet and dry acid deposition.
3. In Activity 3, chalk and zinc simulate manmade structures. Explain the effects of acid rain on calcium carbonate and metal structures. Relate this to your observations.
4. Using the data collected in Activity 4, rank the abilities of the different bedrocks to neutralize acid, from worst to best. What would you expect the pH of surface water in areas containing limestone bedrock to be, compared with areas having granite bedrock?