Acid Precipitation

Introduction

Nearly 70% of the Earth's surface is covered with water. A small portion of this water enters the atmosphere through evaporation and then cycles through it, eventually precipitating out of it in liquid or solid form, and returning to the planetary reservoir. During its time in the atmosphere, water may interact with a number of elements or compounds. Frequently, compounds will dissolve in liquid water and dissociate; solutions of various sorts result. These solutions have differing chemical properties.

Living organisms on this planet need water to survive. They also require a number of other elements and compounds, most in very small quantities. The chemical properties of pure water, and of some of the solutions formed by its interactions with other substances, expedite processes beneficial to them. One of these properties is acidity. Many forms of life have adapted themselves to exploit this natural quality. The slight natural acidity of precipitation, for example, makes available to plants essential minerals normally bound up in rocks.

When precipitation becomes overly acidic, some of its chemical properties become harmful to living things. Acidification of precipitation can happen through the release of acid-forming compounds into the atmosphere via a number of processes; for example, intense volcanic activity. During the past few hundred years, human industrial activity has been a major source of these acid-producing compounds. In certain regions of the world, overly acid precipitation has become a serious problem.

Goals and Key Concepts

By the end of this class, students will:

- Understand what acid precipitation is and how it is produced.
- Be acquainted with the effects of acid precipitation on plants and animals in the Northern Forest.

Vocabulary

Acidic pollutants may be deposited on the Earth from the atmosphere in both wet and dry form. The common term used to describe this process is **acid deposition**. The term **acid precipitation** is used specifically to describe the wet forms of acid pollution that can be found in rain, sleet, snow, fog, (hail, and cloud droplets). An **acid** may be defined as any substance that when dissolved in water dissociates to yield corrosive hydrogen ions. The acidity of substances dissolved in water is commonly measured in terms of **pH** (defined as the negative logarithm of the concentration of hydrogen ions). According to this measurement scale solutions with pH less than 7.0 are described as being **acidic**, while those with a pH greater than 7.0 are considered **alkaline** or **basic**. (The pH scale range is 0 to 14; a pH of 7.0 is defined as neutral.) Precipitation normally has a pH between 5.0 and 5.6 because of natural atmospheric reactions involving carbon dioxide. Precipitation is considered to be acidic when its pH falls below 5.6 (which is 25 times more acidic than pure water).["1"]—*see resources*

The most common ingredients in acidic pollutants are sulfur and nitrogen. **Sulfur**, a yellow non-metallic solid at room temperature and pressure, and **nitrogen**, a colorless gas composing 78% of the Earth's atmosphere, react with oxygen to yield acid-forming **compounds** such as **sulfur dioxide** and **nitrogen oxides**. When these substances enter into solution in water, further reaction with oxygen produces acids that contaminate precipitation. The continual addition of acid precipitation to the soil, or existing bodies of water, may result in their **acidification**.

The first step in reducing the volume of these atmospheric pollutants is to identify their source(s). This is commonly done by sampling the air at a number of locations at specific times. Using wind speed and direction data, the path through the atmosphere taken by the air parcels passing the collection sites may be calculated. This path is referred to as the air parcels' **trajectory**.

["1"]*— see web resources*

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Class Outline

I. Acids and Acidity

An **acid** may be defined as a compound that:

A. Has hydrogen ions that can be replaced by a metal or an electropositive ion group, to yield a salt. One example is the reaction of hydrochloric acid, HCl, with the metal sodium, Na, to give sodium chloride plus hydrogen gas. ($2Na + 2HCl \longrightarrow 2NaCl + H_2$ Sodium chloride is table salt.)

B. Neutralizes alkalis, or bases

C. Usually has a sour taste

D. Turns blue litmus paper red

Activity 1: Acid or Not?

Objective: To discover common substances that are acidic.

The class is divided into groups of 6 to 8 children seated around a table. Each group of students is given strips of neutral (purple) litmus paper to dip into small samples of several common substances to determine whether or not they are acidic. The list of substances may include: milk, bleach, ammonia, orange juice, lemon juice, vinegar, tap water, shampoo, distilled water, soda water, and saliva from their own mouths. Results are recorded on a class chart showing which substances are acidic (red), neutral (purple), or basic (blue).

Acidity is the quality or state of being acid. Many substances are acidic to some degree. The pH scale was developed to quantify the acidity of various substances. "pH" is defined as the inverse logarithm of hydrogen ion concentration, the concentration being measured in gram atoms per liter. The pH scale ranges from 0 to 14, with numbers from 0 through 6.999 indicating progressively lesser degrees of acidity; 7 defined as neutral, and numbers from 7.00 through 14 indicating increasing degrees of alkalinity. Distilled water has a pH of 7. The pH scale is logarithmic: a difference in pH of one unit corresponds to a tenfold change in acidity or alkalinity, a difference of two units to a one hundred-fold change, etc.

Activity 2: Just How Acidic?

Objective: To determine the approximate pH of some common substances.

The substances that tested acidic in Activity 1 are sampled again, by groups of students, this time using a common garden pH test kit or pH dip strip indicators. They are arranged, in a class chart, in pH sequence, from most acidic on the left, to least acidic on the right.

II. Acid Precipitation, and How It Is Produced

Precipitation on Earth consists of water, in liquid or solid form. Distilled water is neutral. Its pH value is 7. Strictly speaking, therefore, acid precipitation is that which has a pH of less than 7. Even "pure" rainwater, or water gained from the melting of snow, sleet, or hail, is slightly acid due to reaction with atmospheric carbon dioxide. A very dilute solution of carbonic acid results, and the rain or melt-water winds up with an average pH of 5.6. So the term "acid precipitation" is usually reserved for precipitation with a pH below 5.6.

Acid precipitation is most commonly produced through chemical reaction of water with nitrogen—or sulfur-containing compounds. Through these reactions, acids of nitrogen or sulfur are created. The reactions are as follows:

A. Sulfur dioxide and water vapor in the atmosphere combine to form sulfurous acid.

$SO_2 + H_2O \longrightarrow H_2SO_3$

Sulfurous acid then reacts with ozone in the atmosphere to produce sulfuric acid and oxygen.

$2H_2SO_3 + 2O_3 \longrightarrow 2H_2SO_4 + 2O_2$

Sulfuric acid is a strong acid and dissolves in cloud droplets.

B. In the atmosphere, nitric oxide reacts with oxygen to form nitrogen dioxide.

$2NO + O_2 \longrightarrow 2NO_2$

Nitrogen dioxide then reacts with water vapor to form a mixture of nitrous and nitric acids.

$4NO_2 + 2H_20 \longrightarrow 2HNO_2 + 2HNO_3$

These nitrogen acids also dissolve in cloud droplets.

"2"—*see book resources*

More than 90% of sulfur-containing compounds in the atmosphere are present due to human activity such as the burning of fossil fuels in power plants, factories, and homes; and the increased use of automobiles. Volcanic eruptions and organic decay account for the remaining small percentage that would be present naturally. Oxides of nitrogen, the precursors of the acids of nitrogen in acid precipitation, are overwhelmingly produced as a result of human activities, primarily fossil fuel combustion. Bacterial action, lightning, volcanic activity, and forest fires account for only around 5% of the total atmospheric load of nitrogen oxides.

Activity 3: Making Acid Rain.

The class is divided into groups of 4 to 5 students around a desk or table. Each group is given a small ceramic plate on which is placed an orange juice can lid, a hood made out of the top half of a large soda bottle with the screw cap removed, a spray bottle of distilled water, and two indicator strips. A small quantity of powdered sulfur is placed on the lid. The students first test and record the pH of the water in the spray bottle. The teacher ignites the sulfur using a portable torch. The students immediately place the plastic hood over the sulfur, and combustion products are allowed to accumulate. The students carefully mist water from the spray bottle into the opening of the hood allowing the fumes to dissolve. Water that collects at the bottom of the container is then retrieved, and its pH sampled. The two pH's are compared..

III. Effects of Acid Precipitation

Considerable research carried out primarily since the early 1970s has led to a growing comprehension of how acid precipitation changes water and soil chemistry. It has been difficult to proceed from that understanding to a clear quantitative assessment of acid precipitation's importance in affecting forest health. Climate change, the arrival or spread of pathogens, and drought are but three of many other processes that have a significant role to play in that area. It is clear, however, that acid precipitation does play a destructive role, and may act synergistically with other pollutants to undermine the health of trees in the Northern Forest, and render them more likely to succumb to other stressors than would otherwise be the case.

A. Background

1. pH History

Precipitation pH of 5.0-5.6 was observed in New England and the Northern Forest region from the inception of such measurements early in the 20th century, until the early 1950s. Rapid acidification took place thereafter-pH's dropped to less than 4.6 by the mid 1950s, to near 4.3 in the mid 1960s, and bottomed out at ~4.0 in the mid 1970s. Since then, there has been a very slow recovery, to a weighted average of about 4.4.

2. Reasons for Acidification

The rapid drop in pH in the region did not take place until shortly after 1950; despite a substantial increase in sulfur and sulfur compound emissions throughout the Ohio Valley beginning in 1900. Through the early 1940s, sulfur emissions due to coal burning were very high, but there was also considerable alkaline material emitted as a constituent of soot particles, and smoke stacks were short. Acidic sulfur compounds were neutralized by the alkaline particles in the soot; because the smoke was vented to the atmosphere relatively close to the ground level, much of the material settled out to the west of New England.

After a brief decline in the late 1940s, the total amount of sulfur emissions surged upwards once again. At the same time, local power companies built taller smoke stacks in response to community complaints, and installed precipitators to intercept soot. With the soot particles taken out of the smoke stream, there was no longer a supply of alkaline material to neutralize the acids produced by the reaction of water with the sulfur compounds; taller smoke stacks enabled the smoke plume to disperse over a much wider area. More coal-combustion by-products were therefore able to reach the Northern Forest; and the acidity of those by-products was much greater due to the in-stack scrubbing of the soot particles. Shortly after 1950, a critical threshold was passed, and the pH of the precipitation plummeted. The load of nitrogen oxides in the regional air stream began rising in the 1950s as well, coincident with a rapid increase both in the number of cars and trucks being driven, and in the number of miles driven per vehicle.

3. Current Situation

The nationwide emission of sulfur and sulfur compounds peaked in the mid- 1970s, with a steady subsequent decrease. In our region, sulfur deposition has decreased ~20% since 1995 alone, thanks to actions mandated by the Clean Air Act of 1990. Sulfuric acid is therefore decreasing as a percentage of the total acid contained in acid precipitation. However, there is still a serious problem. The total deposition of nitrogen compounds and nitric acid has remained steady, or risen slightly since the early 1980s, because of the continued rapid increase in automobile numbers and mileage driven over the past 20 years. This increase has been rapid enough to offset improvements in emission controls.

B. Acid Rain and Water

Acid precipitation's effect on stream and lake pH varies according to the chemical composition of the underlying soil or bedrock. Where acid-neutralizing minerals such as calcium or magnesium are abundant, the acidification of surface water is minimal—the acid-neutralizing minerals act as buffering agents. Even in these areas, during periods of high flow (spring floods or heavy rain storms), the surge of acids may temporarily overwhelm the buffering ability of the neutralizing minerals, and the acidity of the surface water will increase. Once flow returns to normal, acidity will decrease. However, in areas where either the soil or bedrock lacks such buffering agents, acid precipitation will steadily lower the pH of surface waters to a point well below what would be the case if the precipitation were not acidic. Regions with granitic bedrock are very susceptible to having surface waters acidified: such areas include the Adirondacks of New York State, the White Mountains of New Hampshire, and portions of Vermont. In the Adirondacks, surveys show that 41% of the lakes greater than 2.5 acres in size are either acidic year round, or are susceptible to surges of acidification during periods of high water flow.

Surface water acidification affects the ecosystem of the entire water body by altering the population of organisms throughout the food web. Effects are increasingly severe as acidification proceeds. For example: as the water pH approaches 6.0, crustaceans, insects, and some plankton species start to disappear. As the pH approaches 5.0, major changes in the plankton community begin, less desirable kinds of mosses and planktons begin to take over, and a progressive loss of fish populations begins. Below pH 5.0, fish nearly disappear, decomposition of bottom material slows or ceases, and frog populations decline steeply. In general, the eggs or young of most species are more sensitive to acidification than the adults. Thus, for example, the pH of a lake may still be high enough to support a population of adult fish for a time, but those fish will not be able to reproduce successfully. Eventually, the fish population will disappear. Or, the pH of that lake may be high enough to support frogs, but too low for the insects that provide their food. The frogs starve, and the lake becomes frog-free.

C. Acid Precipitation and Plants

By comparison with water, acid precipitation's effects on plants and plant health are less direct and more complex. However, taken as a whole, they are deleterious. Following are four of the best-documented destructive effects of acid precipitation:

1. Acid precipitation increases the rate at which acid-neutralizing minerals are removed from the soil. Two of the most common are calcium and magnesium. The increased rate of removal, or leaching, of these minerals makes them less available to plant roots for uptake. Calcium is a mineral important to plant health—it enables plant cells to maintain their integrity; and acts as a chemical messenger, alerting the plant to the onset of stresses such as drought and cold, thus enabling it to respond quickly and efficiently to such threats.

2. Acid precipitation leaches calcium from the foliage of many tree species. This has been documented for sugar maple, red spruce, balsam fir, white pine, and hemlock, for example. The loss of calcium from foliage, combined with its reduced availability from the soil, increases the chances that a tree will develop a calcium deficiency. When that happens, the tree's response to stress is degraded, and its ability to maintain cell membrane integrity is compromised. It becomes more susceptible to damage due to stress, and a downward spiral in health begins. With red spruce, studies have documented a decrease in cold tolerance of 5 to 21 degrees Fahrenheit following exposure to acid precipitation, thereby increasing its susceptibility to damage from freezing and winter injury. Sugar maple is another species sensitive to calcium and magnesium shortages. Current research indicates that when foliar magnesium in sugar maples falls below a certain threshold, the trees will decline when stressed.

3. Acid precipitation can alter the protective waxy surface of leaves and needles, lowering the resistance of trees to disease and water loss.

4. Acid precipitation can lower the pH of soil sufficiently to make elements toxic to plants, such as aluminum, more soluble. When tree roots take up aluminum in sufficient quantity, their ability to absorb water and other nutrients is progressively destroyed. Without sufficient water, trees will weaken and eventually die.

D. Conclusion

Acid precipitation is a serious problem in eastern North America in general, and the Northern Forest in particular. Its origins are well understood, its destructive effects well documented and increasingly fully comprehended. Ongoing research will add to this knowledge; whether or not it will continue to fall on this region is up to us.

Resources

Suggestions for Teachers

This is a subject that may be explored in some depth through further activities. A series of basic activities may be found at the Environmental Protection Agency's web site on acid rain. Refer to the listing below. More sophisticated activities such as systematic monitoring of the pH of precipitation, by event; the concurrent monitoring of the pH of local streams and ponds; and monitoring the pH of local soils, may be pursued by consulting sources of expertise in your community or state.

Books

These are books geared to the adult reader.
Acid Rain. Boyle, Robert H. and Boyle, R. Alexander. Schoken Books, New York, NY. 1983.
"2"–Atmosphere, Climate, and Change. Crutzer, Paul J. and Graedel, Thomas E. Scientific American Library. W.H. Freeman and Co., New York, NY. 1997.
The Dying of the Trees: The Pandemic in America's Forests. Little, Charles. Viking Penguin, New York, NY. 1995.
Troubled Skies, Troubled Waters: The Story of Acid Rain. Louma, Jon R. Viking Press, New York, NY. 1984.
Last Stand of the Red Spruce. Mello, Robert A. Island Press, Washington, D.C. 1987.
Reading the Forested Landscape. Wessels, Tom. The Countryman Press, Woodstock, VT. 1997.

The following are edited, collectively written treatises organized around a single, broad topic. Published by the National Academy Press, they are excellent, although sometimes technical, summaries of the thinking in the scientific community at the time of their compilation.If not available at local libraries, they may be ordered through the National Academy Press web site at http://books.nap.edu/catalog/
Acid Depostion: Atmospheric Processes in Eastern North America. National Academy Press. 1983.
Acid Deposition: Effect on Geochemical Cycling and Biological Availability of Trace Metals. National Academy Press. 1985.
Acid Deposition: Long Term Trends. National Academy Press. 1986.
Ecological Risks: Perspectives from Poland and the United States. National Academy Press. 1990.

Web Sites:

Samples of the better web sites devoted in part or in whole to the subject of acid precipitation.

From Canada:

1. http://royal.okanagan.bc.ca/mpidwirn/atmosphereandclimate/acidprecip.html "1"— *see site introduction*
2. wysiwyg://384/http://www.ns.ec.gc.ca/aeb/ssd/acid/acidfaq.html
3. http://www.gov.nb.ca/environm/air/

From the United States:

1. http://nadp.sws.uiuc.edu/ National Atmospheric Deposition Site
2. http://www.epa.gov/acidrain E.P.A. Acid Rain Site
3. http://www.enn.com/enn-news-archive/ Environmental News Network Archives
4. http://www.vmc.snr.uvm.edu Vermont Monitoring Cooperative
5. http://www.hbrook.sr.unh.edu Hubbard Brook Research Foundation

Sites containing only lists of links:

1. http://www.econet.apc.org/acidrain
2. http://www.uwsp.edu/acaddept/geog/courses/geog100/Acid-Rain-Resources.htm

List of articles related to acid rain, compiled for a college course run by Professor Thomas Detwyler.

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Organizations

Vermont Monitoring Cooperative

A network of cooperators from government, academic, and private sectors, administered jointly by the State Agency of Natural Resources, the University of Vermont, and the USDA Forest Service, who gather and share information on Vermont's forest ecosystem.

An excellent source for ongoing research into acid deposition/precipitation and its effects on various ecosystems.

111 West Street
Essex Junction, VT 05452
Tel: 802-879-5687
e-mail: sandy.wilmot@anrmail.anr.state.vt.us

Hubbard Brook Research Foundation

Another excellent source for current research into and data on acid deposition /precipitation and its effects on regional ecosystems.

Headquarters:	***Field Office:***
6 Sargent Place	RR 1 Box 791
Hanover, NH 03755	Campton, NH 03227
Tel: 603-653-0390	Tel: 603-726-8911

e-mail: hbrook@hbresearchfoundation.org

Source for Litmus paper and pH dip strips:
Carolina Biological Supply Company
P.O. Box 6010
Burlington, NC 27216-6010
Tel: 1-800-334-5551/ e-mail: carolina@carolina.com

Vermont Standards

This class is associated with the following standards: 7.11 and 7.12

SYSTEMS

Analysis

7.11: Students analyze and understand living and non-living systems (e.g., biological, chemical, electrical, mechanical, optical) as collections of interrelated parts and interconnected systems.

SPACE, TIME, and MATTER

Matter, Motion, Forces, and Energy

7.12: Students understand forces and motion, the properties and composition of matter, and energy sources and transformations.