Pure water has a pH of 7.0 (neutral); however, natural, unpolluted rainwater actually has a pH of about 5.6 (acidic). [Recall from Experiment 1 that pH is a measure of the hydrogen ion (H⁺) concentration.] The acidity of rainwater comes from the natural presence of three substances (CO₂, NO, and SO₂) found in the troposphere (the lowest layer of the atmosphere). As is seen in Table I, carbon dioxide (CO₂) is present in the greatest concentration and therefore contributes the most to the natural acidity of rainwater.

**Natural Acidity of Rainwater**

Carbon dioxide, produced in the decomposition of organic material, is the primary source of acidity in unpolluted rainwater.

**NOTE:** Parts per million (ppm) is a common concentration measure used in environmental chemistry. The formula for ppm is given by:

\[
\text{ppm} = \frac{\text{amount of substance}}{\text{total volume}} \times 10^6
\]
Carbon dioxide reacts with water to form carbonic acid (Equation 1). Carbonic acid then dissociates to give the hydrogen ion (H+) and the hydrogen carbonate ion (HCO3−) (Equation 2). The ability of H2CO3 to deliver H+ is what classifies this molecule as an acid, thus lowering the pH of a solution.

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \quad (1)
\]

\[
\text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^- \quad (2)
\]

Nitric oxide (NO), which also contributes to the natural acidity of rainwater, is formed during lightning storms by the reaction of nitrogen and oxygen, two common atmospheric gases (Equation 3). In air, NO is oxidized to nitrogen dioxide (NO2) (Equation 4), which in turn reacts with water to give nitric acid (HNO3) (Equation 5). This acid dissociates in water to yield hydrogen ions and nitrate ions (NO3−) again lowering the pH of the solution.

\[
\text{N}_2 + \text{O}_2 \xrightarrow{\text{lightning}} 2\text{NO} \quad (3)
\]

\[
\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow \text{NO}_2 \quad (4)
\]

\[
3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO} \quad (5)
\]

**Acidity of Polluted Rainwater**

Unfortunately, human industrial activity produces additional acid-forming compounds in far greater quantities than the natural sources of acidity described above. In some areas of the United States, the pH of rainwater can be 3.0 or lower, approximately 1000 times more acidic than normal rainwater. In 1982, the pH of a fog on the West Coast of the United States was measured at 1.8! When rainwater is too acidic, it can cause problems ranging from killing freshwater fish and damaging crops, to eroding buildings and monuments.

**Sources of Excess Acidity in Rainwater**

What causes such a dramatic increase in the acidity of rain relative to pure water? The answer lies within the concentrations of nitric oxide and sulfur dioxide in polluted air. As shown in Table II and Figure 1, the concentrations of these oxides are much higher than in clean air.
Table II

Humans cause many combustion processes that dramatically increase the concentrations of acid-producing oxides in the atmosphere. Although CO₂ is present in a much higher concentration than NO and SO₂, CO₂ does not form acid to the same extent as the other two gases. Thus, a large increase in the concentration of NO and SO₂ significantly affects the pH of rainwater, even though both gases are present at much lower concentration than CO₂.

<table>
<thead>
<tr>
<th>Nitric oxide</th>
<th>Internal Combustion</th>
<th>0.2 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur dioxide</td>
<td>Fossil-fuel Combustion</td>
<td>0.1 - 2.0 ppm</td>
</tr>
</tbody>
</table>

Figure 1

Comparison of the concentrations of NO and SO₂ in clean and polluted air.

About one-fourth of the acidity of rain is accounted for by nitric acid (HNO₃). In addition to the natural processes that form small amounts of nitric acid in rainwater, high-temperature air combustion, such as occurs in car engines and power plants, produces large amounts of NO gas. This gas then forms nitric acid via Equations 4 and 5. Thus, a process that occurs naturally at levels tolerable by the environment can harm the environment when human activity causes the process (e.g., formation of nitric acid) to occur to a much greater extent.

What about the other 75% of the acidity of rain? Most is accounted for by the presence of sulfuric acid (H₂SO₄) in rainwater. Although sulfuric acid may be produced naturally in small quantities from biological decay and volcanic activity (Figure 1), it is produced almost entirely by human activity, especially the combustion of sulfur-containing fossil fuels in power plants. When these fossil fuels are burned, the sulfur contained in them reacts with oxygen from the air to form sulfur dioxide (SO₂). Combustion of fossil fuels accounts for approximately 80% of the total atmospheric SO₂ in the United States. The effects of burning fossil fuels can be dramatic: in contrast to the unpolluted atmospheric SO₂ concentration of 0 to 0.01 ppm, polluted urban air can contain 0.1 to 2 ppm SO₂, or up to 200 times more SO₂! Sulfur dioxide, like the oxides of carbon and nitrogen, reacts with water to form sulfuric acid (Equation 6).
Sulfuric acid is a strong acid, so it readily dissociates in water, to give an H\(^+\) ion and an HSO\(_4\)^\(-\) ion (Equation 7). The HSO\(_4\)^\(-\) ion may further dissociate to give H\(^+\) and SO\(_4\)^{2\,-}\) (Equation 8). Thus, the presence of H\(_2\)SO\(_4\) causes the concentration of H\(^+\) ions to increase dramatically, and so the pH of the rainwater drops to harmful levels.

\[
\text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4^\text{\(-\)} + \text{H}^+ \quad (7)
\]

\[
\text{HSO}_4^\text{\(-\)} \rightarrow \text{SO}_4^{2\,-} + \text{H}^+ \quad (8)
\]

Environmental Effects of Acid Rain

Acid rain triggers a number of inorganic and biochemical reactions with deleterious environmental effects, making this a growing environmental problem worldwide.

- Many lakes have become so acidic that fish cannot live in them anymore.
- Degradation of many soil minerals produces metal ions that are then washed away in the runoff, causing several effects:
  - The release of toxic ions, such as Al\(^{3\,+}\), into the water supply.
  - The loss of important minerals, such as Ca\(^{2\,+}\), from the soil, killing trees and damaging crops.
- Atmospheric pollutants are easily moved by wind currents, so acid-rain effects are felt far from where pollutants are generated.

Stone Buildings and Monuments in Acid Rain

Marble and limestone have long been preferred materials for constructing durable buildings and monuments. The Saint Louis Art Museum, the Parthenon in Greece, the Chicago Field Museum, and the United States Capitol building are all made of these materials. Marble and limestone both consist of calcium carbonate (CaCO\(_3\)), and differ only in their crystalline structure. Limestone consists of smaller crystals and is more porous than marble; it is used more extensively in buildings. Marble, with its larger crystals and smaller pores, can attain a high polish and is thus preferred for monuments and statues. Although these are recognized as highly durable materials, buildings and outdoor monuments made of marble and limestone are now being gradually eroded away by acid rain.

How does this happen? A chemical reaction (Equation 9) between calcium carbonate and sulfuric acid (the primary acid component of acid rain) results in the dissolution of CaCO\(_3\) to give aqueous ions, which in turn are washed away in the water flow.

\[
\text{CaCO}_3(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Ca}^{2\,+}(\text{aq}) + \text{SO}_4^{2\,-} + \text{H}_2\text{O} + \text{CO}_2 \quad (9)
\]

This process occurs at the surface of the buildings or monuments; thus acid rain can easily destroy the details on relief work (e.g., the faces on a statue), but generally does not affect the structural integrity of the building. The degree of damage is determined not only by the acidity of the rainwater, but also by the amount of water flow that a region of the surface receives. Regions exposed to direct downpour of acid rain are highly susceptible to erosion, but regions that are more sheltered from water flow (such as under eaves and overhangs of limestone buildings) are much better preserved. The marble columns of the emperors
Marcus Aurelius and Trajan, in Rome, provide a striking example: large volumes of rainwater flow directly over certain parts of the columns, which have been badly eroded; other parts are protected by wind effects from this flow, and are in extremely good condition even after nearly 2000 years!

Even those parts of marble and limestone structures that are not themselves eroded can be damaged by this process (Equation 9). When the water dries, it leaves behind the ions that were dissolved in it. When a solution containing calcium and sulfate ions dries, the ions crystallize as CaSO$_4$•2H$_2$O, which is gypsum. Gypsum is soluble in water, so it is washed away from areas that receive a heavy flow of rain. However, gypsum accumulates in the same sheltered areas that are protected from erosion, and attracts dust, carbon particles, dry-ash, and other dark pollutants. This results in blackening of the surfaces where gypsum accumulates.

An even more serious situation arises when water containing calcium and sulfate ions penetrates the stone's pores. When the water dries, the ions form salt crystals within the pore system. These crystals can disrupt the crystalline arrangement of the atoms in the stone, causing the fundamental structure of the stone to be disturbed. If the crystalline structure is disrupted sufficiently, the stone may actually crack. Thus, porosity is an important factor in determining a stone's durability.

Additional Links:

- Click here to view the U.S. Geological Survey's excellent site on acid rain.
- The Environmental Protection Agency's site on acid rain presents the basics of this problem in an accessible format.
- The National Atmospheric Deposition Program features isopleth maps showing the concentrations of many different pollutants throughout the country.
- Another very interesting EPA site on acid rain explains the novel "allowance trading system" strategy for getting companies to control their sulfur dioxide emissions.

References:


Acknowledgements:

The authors thank Dewey Holten (Washington University) for many helpful suggestions in the writing of this tutorial.

The development of this tutorial was supported by a grant from the Howard Hughes Medical Institute,