



Acid Rain and Our Nation's Capital

by Elaine McGee



Marble surfaces exposed to rain develop a rough "sugary" texture because the calcite grains are loosened as the edges dissolve in the rain water. Column capital volute, Jefferson Memorial, Washington, D.C.

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A summer rain storm in Washington, D.C.
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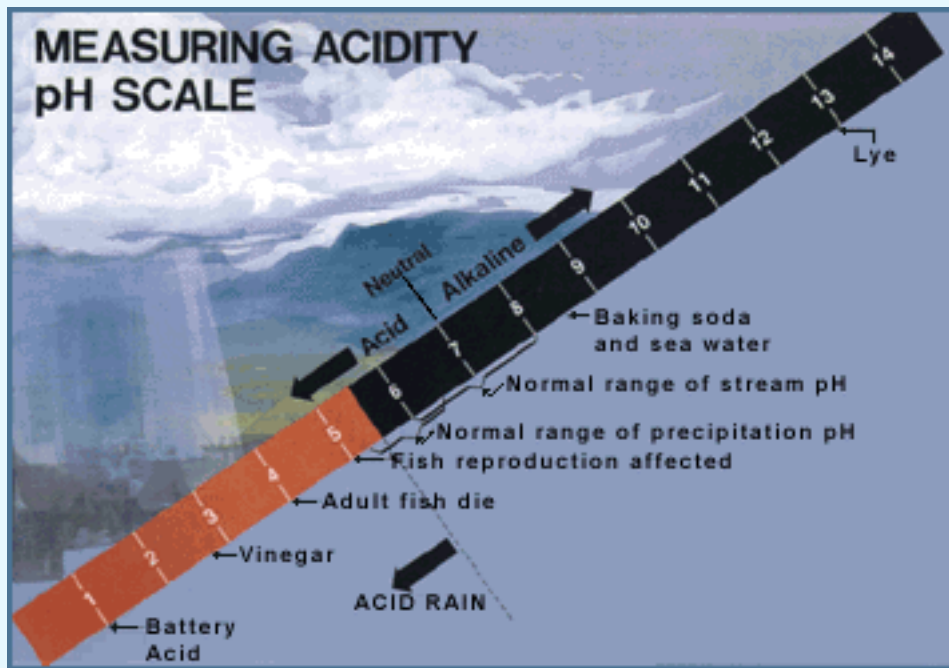
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When polluted air mixes with rain, snow, and fog, acid precipitation forms. This acidity has caused people to worry about the environment; some reports show that acid rain has affected lakes, trees, and fish populations in the Northeastern United States and Canada. Another concern is its effect on historic buildings and monuments.

This booklet focuses on acid rain and its impact on our Nation's capital. Rain in Washington, D.C., has an average acidity of 4.2, about as acid as a carbonated drink and more than ten times as acid as clean, unpolluted rain. This booklet will define acid rain, explain what effects it has on marble and limestone buildings, and show, on a walking tour, some of the places in our Nation's capital where you can see the impact of acid precipitation.



The pH scale:

pH = 7 is neutral, neither acid or alkaline;
smaller pH values are acid, larger pH values are alkaline.
A liquid with a pH of 3 is ten times as acid as one with a pH of 4.

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What is acid rain?

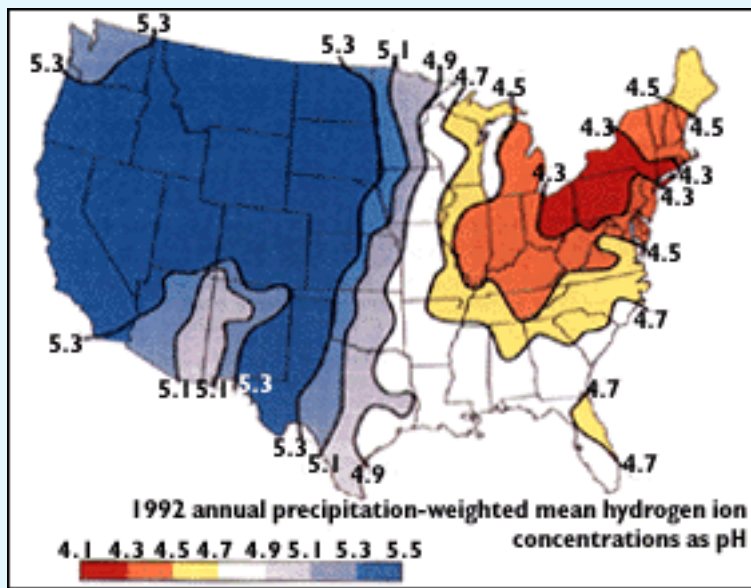
The term "acid rain" is commonly used to mean the deposition of acidic components in rain, snow, fog, dew, or dry particles. The more accurate term is "acid precipitation." Distilled water, which contains no carbon dioxide, has a neutral pH of 7. Liquids with a pH less than 7 are acid, and those with a pH greater than 7 are alkaline (or basic). "Clean" or unpolluted rain has a slightly acidic pH of 5.6, because carbon dioxide and water in the air react together to form carbonic acid, a weak acid. Around Washington, D.C., however, the average rain pH is between 4.2 and 4.4.

The extra acidity in rain comes from the reaction of air pollutants, primarily sulfur oxides and nitrogen oxides, with water in the air to form strong acids (like sulfuric and nitric acid). The main sources of these pollutants are vehicles and industrial and power-generating plants. In Washington, the main local sources are cars, trucks, and buses.



Wet and dry bucket collector, used to collect samples for measuring rainfall acidity.

Acidity in rain is measured by collecting samples of rain and measuring its pH. To find the distribution of rain acidity, weather conditions are monitored and rain samples are collected at sites all over the country. The areas of greatest acidity (lowest pH values) are located in the Northeastern United States. This pattern of high acidity is caused by the large number of cities, the dense population, and the concentration of power and industrial plants in the Northeast. In addition, the prevailing wind direction brings storms and pollution to the Northeast from the Midwest, and dust from the soil and rocks in the Northeastern United States is less likely to neutralize acidity in the rain.



A pH distribution map shows areas in the continental United States of greatest acidity in the rain.

When you hear or read in the media about the effects of acid rain, you are usually told about the lakes, fish, and trees in New England and Canada. However, we are becoming aware of an additional concern: many of our historic buildings and monuments are located in the areas of highest acidity. In Europe, where buildings are much older and pollution levels have been ten times greater than in the United States, there is a growing awareness that pollution and acid rain are accelerating the deterioration of buildings and monuments.

Stone weathers (deteriorates) as part of the normal geologic cycle through natural chemical, physical, and biological processes when it is exposed to the environment. This weathering process, over hundreds of millions of years, turned the Appalachian Mountains from towering peaks as high as the Rockies to the rounded knobs we see today. Our concern is that air pollution, particularly in urban areas, may be accelerating the normal, natural rate of stone deterioration, so that we may prematurely lose buildings and sculptures of historic or cultural value.

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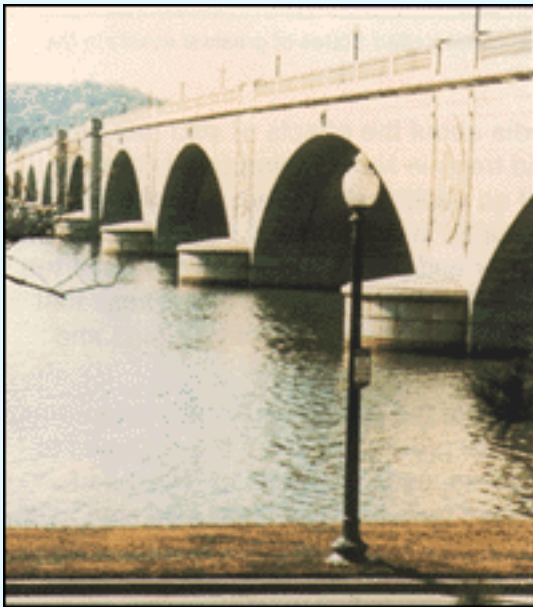
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What about buildings?

Many buildings and monuments are made of stone, and many buildings use stone for decorative trim. Granite is now the most widely used stone for buildings, monuments, and bridges. Limestone is the second most used building stone. It was widely used before Portland cement became available in the early 19th century because of its uniform color and texture and because it could be easily carved. Sandstone from local sources was commonly used in the Northeastern United States, especially before 1900. Nationwide, marble is used much less often than the other stone types, but it has been used for many buildings and monuments of historical significance. Because of their composition, some stones are more likely to be damaged by acidic deposition than others. Granite is primarily composed of silicate minerals, like feldspar and quartz, which are resistant to acid attack. Sandstone is also primarily composed of silica and is thus resistant. A few sandstones are less resistant because they contain a carbonate cement that dissolves readily in weak acid. Limestone and marble are primarily composed of the mineral calcite (calcium carbonate), which dissolves readily in weak acid; in fact, this characteristic is often used to identify the mineral calcite. Because buildings and monuments made of limestone and marble are more likely to be damaged by acid precipitation, they are the main focus of this booklet.



Memorial Bridge in Washington, D.C., is made of granite, the most widely used stone type.



Marble used as a trim on the First Bank in Philadelphia, Pennsylvania.

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How do you recognize limestone and marble?

The main difference between limestone and marble is that limestone is a sedimentary rock, typically composed of calcium carbonate fossils, and marble is a metamorphic rock. Limestone forms when shells, sand, and mud are deposited at the bottom of oceans and lakes and over time solidify into rock. Marble forms when sedimentary limestone is heated and squeezed by natural rock-forming processes so that the grains recrystallize. If you look closely at a limestone, you can usually see fossil fragments (for example, bits of shell) held together by a calcite matrix. Limestone is more porous than marble, because there are small openings between the fossil fragments. Marble is usually light colored and is composed of crystals of calcite locked together like pieces of a jigsaw puzzle. Marble may contain colored streaks that are inclusions of non-calcite minerals.



Limestone is made of fossil fragments, held together with calcite; the shell near the center is about 1 cm across. Botanic Gardens building Washington, D.C.



Marble is made of calcite crystals (white) and some colored grains of mica inclusions; the grains in a marble are locked together like jigsaw puzzle pieces.

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How does acid precipitation affect marble and limestone buildings?

Acid precipitation affects stone primarily in two ways: *dissolution* and *alteration*. When sulfurous, sulfuric, and nitric acids in polluted air react with the calcite in marble and limestone, the calcite dissolves. In exposed areas of buildings and statues, we see roughened surfaces, removal of material, and loss of carved details. Stone surface material may be lost all over or only in spots that are more reactive.

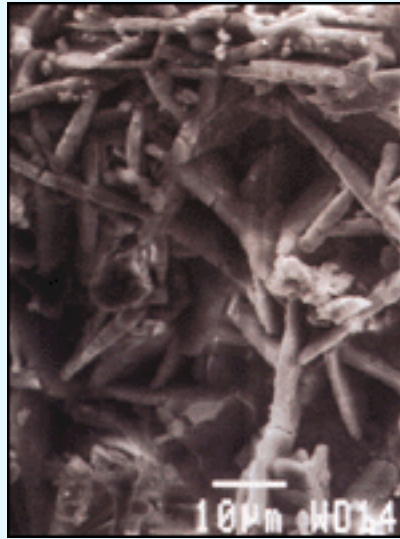
You might expect that sheltered areas of stone buildings and monuments would not be affected by acid precipitation. However, sheltered areas on limestone and marble buildings and monuments show blackened crusts that have spalled (peeled) off in some places, revealing crumbling stone beneath. This black crust is primarily composed of gypsum, a mineral that forms from the reaction between calcite, water, and sulfuric acid. Gypsum is soluble in water; although it can form anywhere on carbonate stone surfaces that are exposed to sulfur dioxide gas (SO_2), it is usually washed away. It remains only on protected surfaces that are not directly washed by the rain. Gypsum is white, but the crystals form networks that trap particles of dirt and pollutants, so the crust looks black. Eventually the black crusts blister and spall off, revealing crumbling stone.



When marble is exposed to acidic rain, sharp edges and carving details gradually become rounded. Antefixes, roof of the Philadelphia Merchants' Exchange (built in 1832).



Blackened crusts on sheltered portions of the limestone Chicago Tribune Building, Chicago, Illinois.



Formed as a result of air pollution, gypsum alteration crusts have blackened, blistered, and spalled from a marble baluster at the Organization of American States building, Washington, D.C.

Scanning electron microscope photograph of gypsum crystals with dirt and pollution particles trapped by the network of crystals. The scale bar is 10 micrometers long.



A marble column at the Merchants' Exchange in Philadelphia shows loss of material where the stone is exposed to rain and blackening of the stone surface where the stone is sheltered from rain.

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Where can we see the effects of acid precipitation?

Washington's buildings and monuments use many different stone types. Marble and limestone buildings are the most likely to show damage, because they are more affected by acidic precipitation and urban pollution. As you follow the tour described in this book, see how granite and sandstone buildings compare with the marble and limestone in the same environment.

This guide will help you recognize some geologic features of buildings, in addition to their historical and architectural aspects, wherever you travel. However, remember one important point when examining buildings and monuments for deterioration: stone deterioration has many causes. Although acid precipitation and urban pollution can accelerate stone deterioration, people, pigeons, and other organisms may also harm our stone structures. In addition, the process of weathering has been going on since the Earth first had an atmosphere. Although we can observe deterioration of the stone, it is hard to determine how much of the deterioration is from acid precipitation and how much is from other causes.



Pigeons sitting on the statue heads have created distinctive deterioration on this building.



Flowers and grasses have grown in the cracks between stones on this church.



This limestone column in the Lincoln Memorial is darkened and dirty from people's hands touching the stone.



Microorganisms have caused this stain to appear on a marble column at the Jefferson Memorial.

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What are we doing about acid rain?

Scientists from many disciplines are studying acid precipitation and its impact. The National Acid Precipitation Assessment Program (NAPAP), a Federal program involving representatives from more than a dozen Federal agencies, has sponsored studies on how acid rain forms and how it affects lakes, crops, forests, and materials. Because buildings and monuments cannot adapt to changes in the environment, as plants and animals can, historic structures may be particularly affected by acid precipitation. Scientists are studying effective control technologies to limit the emissions from power plants and automobiles that cause acid rain. The impact and usefulness of regulations that would require limits on air pollution are also being studied. Finally, scientists are examining the processes of deterioration to find effective ways to protect and repair our historic buildings and monuments. Agencies like the National Park Service, which are charged with protecting and preserving our national heritage, are particularly concerned not only about the impact of acid rain but also about making the best choices for maintaining and preserving our historic buildings and monuments.



Beginning in 1984, the National Acid Precipitation Assessment Program sponsored exposure site studies of limestone and marble, to examine the contribution to stone deterioration that comes from acid precipitation.

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