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ANUPOATED RAIN ON ACIO RAIN

AN UPDATED PERSPECTIVE ON ACID RAIN

Prepared by
Alan W. Katzenstein
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ACID RAIN

FOREWORD

FACT: Some coal-burning power plants emit large amounts of sulfur dioxide and nitrogen oxides.

FACT: Sulfur dioxide and nitrogen oxides react with oxygen and moisture to form sulfuric and nitric acids.

FACT: Rain is sometimes more acidic than generally expected or accounted for.

QUESTION: How do power plant emissions affect the acidity of rainfall?

QUESTION: Is it possible that power plant emissions are *not* the primary cause of "acid rain"?

QUESTION: Is it possible that rain is naturally more acidic than had been expected and that it has been this acidic, to varying degrees, for scores and hundreds and even thousands of years?

It is easy to look at circumstantial evidence and draw conclusions on the acid rain issue. But as new facts develop, a more balanced perspective emerges, furthering our understanding of this complex and controversial matter.

Edison Electric Institute thinks you ought to know all of the facts, new facts as well as older ones, before you decide for yourself. We hope this overview helps clarify some of the troublesome aspects and conveys a better awareness of the naturalness of acidity in the world around us.

BACKGROUND

cid rain is one of the major environmental issues of the early 1980s. The term implies unnaturalness and danger. It creates fears in many people. It rouses strong reactions from fishermen, ecologists and politicians. The term conjures up images of destruction and damage far beyond anything documented to date.

The acidity of rain became a matter of concern in the late 1960's when Swedish scientists claimed that sulfur dioxide emissions from industrial sources, particularly from Great Britain, had adverse effects in Sweden. Some Norwegians soon joined in the allegations that industrial emissions were causing problems for fish, vegetation and human health.

By the early 1970s, problems were reported in the United States, allegedly associated with the acidity of precipitation here. Two U.S. researchers, analyzing data from studies made in the 1950s, 1960s and 1970s, concluded that rainfall in the eastern U.S. had been growing increasingly acidic from one decade to the next and the areas of increased acidity were expanding. The acid changes were attributed to the large amounts of sulfur and nitrogen oxides emitted from heavily industrialized regions in the Midwest.

Is there a direct connection between industrial activity and acid rain?

Most fossil fuels contain sulfur compounds. Refiners remove most of the sulfur from oil and sell it as a by-product, but the sulfur in coal is more difficult to remove. Even "washed coal" typically retains as much as three-fourths of its sulfur. During combustion, the sulfur or its compounds react with oxygen to form sulfur dioxide (SO₂), which is emitted from the chimney or stack. Once in the atmosphere, SO₂ reacts with water and oxidizing agents, and through a series of steps can finally convert to sulfuric acid and other compounds. The conversions vary widely, depending on time, temperature, amount of sunlight and other factors. Some chemists have estimated that as much as half the SO₂ will have been converted after two days in the atmosphere.

New facts and new interpretations of natural events are helping to change that impression and are shaping a new understanding of the nature of acidic rain and of acidity in the environment

Nitrogen, which makes up about 80 percent of the air around us, reacts in the combustion chamber to form a variety of nitrogen oxides (NO_x) which also can convert to a number of other chemical forms including nitric acid.

Both sulfuric and nitric acids are soluble in the water droplets that make up clouds, fog and rain. Some of the acid molecules are dissolved before the droplets fall as rain; others are washed from the air by passing raindrops.

Gases and particles in the upper atmosphere may be carried long distances by moving air masses, during which time they may react and interact, depending upon the amount of sunlight, ozone and other reactive materials present.

The U.S. Environmental Protection Agency has estimated that at the start of the 1970s, about 26 million tons of SO₂ and about 17 million tons of NO_x were emitted annually into the skies of the U.S. Of these totals, about 16 million tons or 62 percent of the SO₂ and about 5 million tons or 29 percent of the NO_x were said to come from fossil fuel-burning electric plants throughout the country.

These quantities are impressive, and concerned groups sought ways to reduce them. Taking a cue from the successful programs that cleared the smoke from the skies of industrial cities, environmentalists, EPA and others proposed that major emitters of SO₂ and NO_x be required to cut those emissions to a minimum.

Stories about acid rain have been told numerous times. Most people have heard only that acid rain is a man-made problem that threatens the environment. New facts and new interpretations of natural events are helping to change that impression and are shaping a new understanding of the nature of acidic rain and of acidity in the environment. This review is designed to provide an updated perspective for all who are concerned.

DEFINED

cid rain is generally defined as rain whose acidity is lower than pH 5.6. But as a subject of national concern, it is important to define it a bit more closely and to exclude some phenomena the popular media have included under the "acid rain" heading.

The issue is sometimes confused by the loose use of the term when referring to other kinds of acidic deposition, such as the "acid smut" from chimnevs and smoke stacks of industrial and chemical plants. The acid smut particles tend to be fairly large and fall to earth within a few miles of the point of origin. Rain is not usually involved in acid smut incidents.

Damage to architectural stone surfaces has been associated with atmospheric pollution, but the major cause appears to be the impact from local sources such as heavy vehicular traffic and nearby oil refining and industrial activity.

Acidic compounds can be precipitated in rain or snow or deposited in dry form. For this review the popular term "acid rain" is used without qualification and where appropriate applies to precipitation. dry deposition, or both.

EXPLAINED

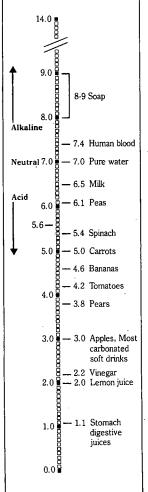
H is the chemists' system for expressing the acidity of water solutions in terms of the concentration of hydrogen ions. On the scale that goes from extremely alkaline pH 14 to extremely acid pH 0, the neutral

point is pH 7.0. All values lower than pH 7.0 are acidic; all above pH 7.0 are alkaline or basic. The lower the pH, the greater the acidity.

Technically, pH is defined as the negative logarithm of the hydrogen ion [H+] concentration as measured in equivalents per liter. The scale is logarithmic, so each successive pH unit represents a 10-fold change in the concentration of hydrogen ions. Doubling or halving the acidity, which means doubling or halving the concentration of hydrogen ions, changes the pH by 0.3 units. For a solution that contains 2.5 microequivalents (.0000025 equivalents) of hydrogen ions per liter, the pH is 5.6. Doubling the [H⁺] to 5 microequivalents lowers the pH to 5.3.

EVERY-DAY LIFE

pH Values of **Familiar Materials**



hemicals are part of every living plant and animal, and many of these chemicals are acidic.

In our vocabulary, "acid" often implies strong actions, such as "acid test", or even unpleasantness, such as "acid tongued." But acids are not necessarily undesirable, unpleasant, harsh or a hazard to life.

Amino acids are the building blocks from which the body makes protein and other tissues. The same lactic acid that helps make some of our popular foods can also be a by-product of energy production in marathon runners and others engaged in vigorous exercise. Ascorbic acid, better known as vitamin C, is one of our dietary essentials. Citric acid gives oranges, lemons and limes their familiar tang, malic acid gives apples their characteristic taste.

Taste is our most sensitive detector of the acidic nature of substances we contact in daily life, but it often deceives us. It is not surprising to find that tomatoes are acidic but most people are surprised to learn that a delicious pear can be more acidic than a tomato or that bananas and carrots are nearly as acidic. All of these have pH values well in the range of the rain that is the subject of scare headlines in the popular media.

NATURE'S WAY

he never-ending cycle of moisture evaporating from the surface of the earth and returning from the skies as precipitation is very much like the process for making distilled water in the laboratory. Rain might be expected to have the same characteristics as distilled water, including a neutral pH of 7, except that the envelope of air surrounding the globe contains many more substances than the gases in a laboratory still.

The ocean of air around us contains about 0.03 percent carbon dioxide (CO₂). CO₂ dissolves in water to form carbonic acid, so it is readily expected that atmospheric moisture will absorb CO₂. form carbonic acid and thus be acidic. Since the pH of a water solution of carbonic acid at 20°C (68°F) is 5.6, many observers have contended that the pH of "clean rain" should be the same as that for carbonic acid.

The atmosphere, however, carries much more than water vapor, condensed moisture and CO₂. Large amounts of sulfur oxides are emitted from volcanos, geysers and other geologic sources. Bacterial activity in the soil and near the surface of ocean and inland waters also creates volatile sulfur compounds. It has been estimated that 60 percent of the world's total atmospheric burden of sulfur compounds is from natural sources.

Large amounts of naturally produced nitrogen oxides and nitrates are also found in the atmosphere. Bacterial activity in the soil generates volatile nitrogen compounds from fertilized soils and decaying proteins. Forest fires produce NO_x, and every lightning flash creates significant amounts of nitric acid.

Lightning's contribution to the acidity of rain has been calculated by several investigators. One estimates that two strokes of lightning over 1 square kilometer (about 4/10 sq. mi.) will produce enough nitric acid to make 2 cm (about 8/10ths of an inch) of rain have a pH of 3.5. Another scientist has calculated that lightning creates enough nitric acid so that annual rainfall over the world's land surfaces would average pH 5.04 without even accounting

for contributions from other natural sources of acidity. Combining the effect of lightning-induced nitric acid and carbonic acid would result in a pH around 4.8.

The ocean of air also carries acid-neutralizing materials such as calcium and magnesium compounds from soil and nitrogen compounds such as ammonia from the natural decay of protein materials.

The chemically active substances in this mixed load can interact with each other to form still other materials. As a result, no single inventory can adequately describe the variable contents of the atmosphere, and no single number can accurately define the pH of "clean" rain.

One fact is certain from the above: designating pH 5.6 for "clean" rain is not very realistic.

What is realistic? The best approach is to look at the rain in places where it is least exposed to the products of industrial activity and fossil fuel combustion. The scientific literature, covering observations from many researchers in many parts of the world, shows rainfall varies widely in acidity, with most of the reported values being well below pH 5.6; that is, more acidic.

☐ In the forest areas of Brazil at the headlands of the Amazon River, an area remote from civilization, the monthly average of 100 rain events in the 1960s ranged from pH 4.3 to pH 5.2, with the median value of pH 4.6 and one reading as low as pH 3.6.

 \Box In the Venezuelan region of the Amazon basin in 1979, 23 rain events averaged pH 4.65.

☐ The rainfall from two hurricanes in September, 1979 sampled at six stations from Virginia to upstate New York, averaged pH 4.5, with one reading as low as pH 3.6. Much of the weather came directly from the Atlantic Ocean and was quite unlikely to have been affected by emissions from any industrial activity.

 $\hfill\Box$ On the island of Hawaii, remote from all industrial activity, the weighted average of precipitation

over a 4-year period was pH 5.3, with a minimum value of pH 3.8. During a 3-year period, the rainfall at a sea level station averaged pH 5.2, while at a station at 11,000 feet elevation, the rain averaged pH 4.2.

 \Box On the South Seas island of Pago Pago, the average pH has been reported as 5.7, with a low reading of pH 4.3.

 \Box In heavy thunderstorm activity at the start of the monsoon season in the remote northern territory of Australia, the rain has averaged between pH 3.4 and 4.0.

☐ The Global Precipitation Network recently reported the following range of readings:

Indian Ocean pH 3.98—5.26 Alaska pH 4.54—5.50 Australia pH 4.0—5.0 Bermuda pH 3.5—6.0

Rainfall in remote regions of the world is clearly often below pH 5.6. While there are exceptional readings below pH 4 and above pH 6, the average values tend to fall in the range of pH 4.5–5.5. Thus, it is questionable whether pH 5.6 is realistic for defining "clean rain" or even whether any single value should ever be designated as a reference point.

Awareness of the acidic nature of rain is not new. As early as 1852, a French scientist noted measurable quantities of nitric acid and nitrogen compounds in the rain of Paris. In 1872, the acidic nature of rain was documented in a lengthy book on the chemistry of English rain.

Additional evidence is available from ice samples from Greenland. Analyses show that many times in the last 7,000 years, precipitation was well below pH 5.6, even below pH 5.0. These acidic periods correspond to the times of known volcanic eruptions, most of them several thousand miles from Greenland. In some cases, the periods of extra acidity lasted for a year or more; not surprising since a major eruption can toss millions of tons of material high into the atmosphere to circle the earth for many years.

One fact is certain from the above: designating pH 5.6 for "clean" rain is not very realistic This and other evidence make clear that no single pH value can adequately define the natural acidity of rain

The sediment in Scandinavian lakes reveals levels of acidity more than 800 years old that are far greater than experienced today.

This and other evidence make clear that no single pH value can adequately define the natural acidity of rain, but it is very often much lower than pH 5.6. More and more scientists have been questioning pH 5.6 as the appropriate figure. It seems likely the "natural" pH of rain eventually will be accepted as falling around pH 4.5–5.0 with no single figure being designated.*

WHAT DETERMINES THE ACIDITY OF RAIN?

Sulfates and nitrates come from both natural sources and human activity much more than simply condensed water vapor plus absorbed carbon dioxide.

Droplets cannot form until there are solid particles on which the vapor can condense. The nuclei for raindrops are infinitesimal airborne particles of dust blown from the earth's surface and salts from sea spray. The dust particles, in particular, often have the same acid-neutralizing calcium

he raindrop is a complex chemical broth—

and magnesium content as soils from Kansas to Kenva.

Acids and alkalis neutralize each other in solution, so the carbonic, sulfuric and nitric acids in condensed droplets start to react with the calcium, magnesium and other alkaline materials in the nuclei. The extent of neutralization depends on the amounts present, the time they have to react and other factors.

Dozens of chemical substances can be found in rain surface waters, but only those which ionize in solution affect the hydrogen ion concentration; that is, the acidity of the liquid. Eight of these substances suffice to adequately measure the acidity of rain. Three are known as "anions" because they have negative ion charges: sulfate (SO_4^{--}) , nitrate (NO_3^{--}) , and chloride (CI^{-}) . The remaining five are known as "cations" because they have positive ion charges: calcium (Ca^{++}) , magnesium (Mg^{++}) , ammonium (NH_4^{++}) , sodium (Na^{++}) and potassium (K^+) .

When the concentrations of the eight ions have been determined, the net balance between positive and negative ions is counted as microequivalents of hydrogen ions (H⁺), whose concentration in the solution defines its acidity.

Where do the eight materials come from?

As noted earlier, sulfates and nitrates come from both natural sources and human activity. Bacteria in the soil and in surface waters produce volatile sulfur compounds, but so do volcanoes, geysers and other geologic activities. The sulfur in fossil fuels is converted to gaseous sulfur dioxide when coal and oil are burned. Total sulfur emissions worldwide are estimated at around 200 mil-

^{*}Variation in nature is well known and widely accepted in other matters. For example, 98.6°F is usually said to be the "normal" body temperature. But medical references show the range from 96.4° to 99.1° as the normal limits, and most physicians would consider occasional deviations outside that range quite acceptable.

lion tons a year or more, with a substantial portion of this amount generated by natural sources.

The nitrogen compounds are produced by bacterial activity in the soil and decaying matter, from forest fires and lightning, and from the combustion of fuels that include not only coal and oil but also gas and wood and even from the burning of crop residues on farms and fields from Jamaica to Jakarta.

Both sodium and chloride come primarily from the salt in sea spray that is swept into the air and eventually to high altitudes to be carried long distances. Calcium, magnesium and potassium are primarily from surface soil particles.

Once these and other chemicals dissolve, they lose their chemical identity. The net balance of ions determines the acidity of the solution, and it is misleading to suggest that any contributing acids are still present as such. No one would think of saying that a dilute solution of table salt in water contains hydrochloric acid or sodium hydroxide. It is similarly misleading to say that rain or lake water contain sulfuric or nitric acids, even though the pH is less than 7.0 and the sulfate and nitrate present may have come largely from the respective acids formed by conversion from SO₂ and NO_x.

MEASUREMENT OF pH

Comparing reports from different sources using different methods can lead to erroneous conclusions about trends in acid precipitation

hemists have several ways to measure the acidity of solutions. Unfortunately, these methods of determining pH can give differing results. Furthermore, for some of the simpler methods, it is evident that pH values from different laboratories do not always agree with each other. Consequently, comparing reports from different sources using different methods can lead to erroneous conclusions about trends in acid precipitation.

Before the 1960s the most common method of determining pH was the use of special dye indicators and comparing the color changes of a sample against standardized color references. The results were not very precise by today's criteria, but the procedure was simple and frequently used, particularly in the field.

More precise and much easier is the use of a pH meter whose sensitive electronic probes are simply dipped into the solution in question and the pH value read directly from the meter. Unfortunately, pH meters are subject to damage and need frequent recalibration. For the most accurate results, they should be used with controlled temperature, usually not possible in field work.

The pH value can be determined by titration in which the chemist measures the amount of a known alkaline solution needed to neutralize the acidity of an unknown liquid. This is more complicated than using a pH meter but can yield very precise results. As with the other methods, titration fails to provide clues as to what components in the solution contributed to its acidity.

Most precise and most informative, but also by far the most complicated procedure, is determining the quantity of each of the principal ions in the solution. For rain, this involves measuring all eight of the ions discussed previously. Complete ion analysis is the preferred method today for gaining maximum information about the make-up and probable contributors to the acidity of rain or lake water samples.

It would be nice if all four methods gave the same final pH value, so investigators could com-

pare with validity data obtained by different methods. It is known now, for example, that the color comparison technique used 20 or more years ago gave results 1 to 1½ pH units too high. Comparing a colorimetric pH value against one obtained by a different technique can suggest differences in acidity that are entirely false.

In a 1980 report on 849 Adirondack lakes, two New York environmental researchers recognized the questionable reliability of pH data reported prior to 1975, and concluded these values should be disregarded in compiling a data base for measuring trends of acidity of Adirondack lakes.

How reliable are the values obtained by the simple pH meter? When laboratories of the World Meteorological Organization network analyzed identical samples of artificial rain, the results averaged 0.63 pH units too low—4 times more acid than the true value. What is more, their reports showed spreads of 1.90 to 3.37 pH units between the highest and lowest readings for the various samples. A study among a group of U.S. laboratories showed similar errors, again tending to report results more acidic than the true values. The pH meter is a dependable instrument, but reports of pH values may not be compared validly unless the quality of the laboratory work has been established.

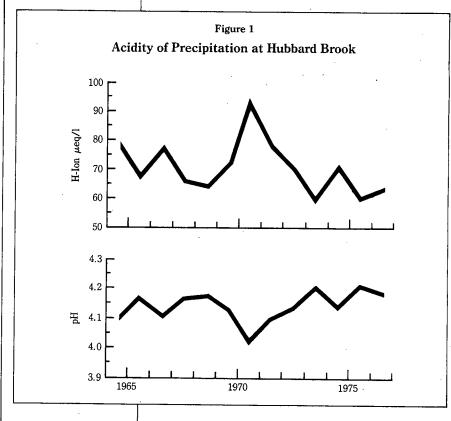
With the knowledge of these shortcomings becoming increasingly widespread, scientists are taking greater care in selecting the data from which comparisons are made.



espite some statements, the available evidence certainly is not consistent with the charge that rain is becoming increasingly acidic.

It is true that the acidity of rain varies from time to time and from place to place. But where the data cover a substantial period, no real trends can be shown.

The longest continuous record of precipitation chemistry in the United States is from Hubbard Brook, a research station in north central New Hampshire. Data collected since 1963 show fluctuations in rain pH from week to week and year to year. But no long term trends, either up or down, can be found either in the charted annual averages (Figure 1) or in statistical analyses of the weekly readings.



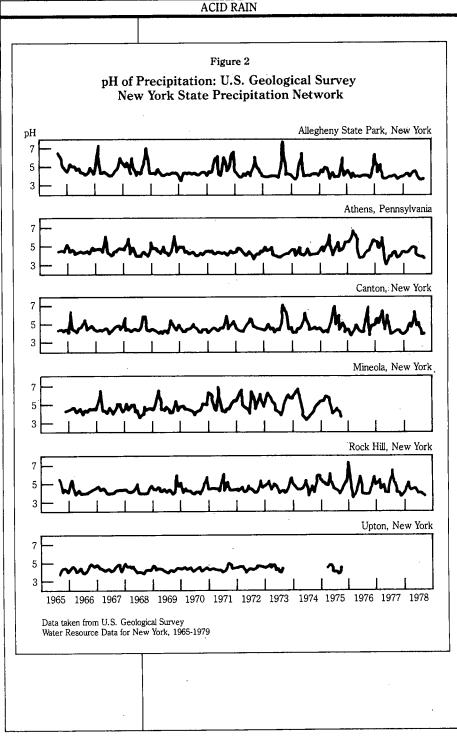
Continuous data from many more locations but for a few less years are those of the U.S. Geological Survey at nine stations in and around New York State from 1965 through 1978. The charts drawn from the USGS data show clearly the continuing variability of precipitation pH but the absence of trends (Figures 2 and 4).

Since it is now clear there are no significant trends in acidity that can be supported by reliable data, how did the idea that the nation and the world have an acid rain problem get its start?

In the mid-1970s, two Cornell University scientists looked at data that suggested acidity had increased in the eastern U.S. between the mid-1950s and the mid-1970s. Publicity about their conclusions preceded confirmation of their work, and it has been difficult to stem the flow of impressions based on their early reports.

A group at the Illinois State Water Survey, however, has found an explanation for at least part of the acid rain variability in the Midwest. From the records available in Illinois, it was learned that the sulfate and nitrate content of the rain had changed hardly at all over the 20 year span, but the calcium and magnesium levels had been much higher in the mid-50s than in the mid-70s. The 1950s had been a period of drought and dust storms in the Midwest, so the rain indeed was more acidic in the 1970s than in the 1950s. The increased acidity, however, is attributable not to changes in sulfates and nitrates, but rather to the unusually high levels of acid-neutralizers present in the earlier period.

Differences in acidity of rain on an area basis were explained by a look at the detailed chemistries of current patterns in Illinois against those in New York. Scientists at New York's Atmospheric Sciences Research Center recently showed that the rain in Illinois in the summer half of 1978 was less acidic than the rain that fell in upstate New York. The sulfate and nitrate depositions in the two regions were remarkably similar, but Illinois rain contained more calcium than that in New York, accounting for the differences in acidity in the two regions.



It is premature to assert that rainfall is not increasing in acidity anywhere Some of the impressions of increasingly acid rain may well have arisen from comparisons of data obtained by different methods, with the tendencies to detect differences due to the method of analysis rather than the rain itself.

It is premature to assert that rainfall is not increasing in acidity anywhere. But not one of the reports of increasing acidity has stood up under scientific challenge. In cases where the underlying data are most complete—Hubbard Brook and the USGS studies around New York State—the evidence certainly points to variability, but fails to support stories that the rain is becoming increasingly acidic.

LONG RANGE TRANSPORT OR LOCAL SOURCES eather generally moves from west to east in the United States, so it was natural to suspect that emission products from the industrial Midwest might move on prevailing winds to New York, New England and even into Canada.

Serious attempts to confirm a linkage between midwestern emissions and eastern depositions have created thorny problems of research that have increasingly called for complex computer models to analyze the emission products, their interaction and their ultimate fate. At mid-1981, the Environmental Protection Agency concluded, "the state of the art" of long-range transport modeling is not sufficiently advanced to determine the causes or the sources of interstate pollution.

While some investigators focused on a search to explain long range transport of midwestern coalburning by-products, others have looked at the role of oil burning nearer to the places where acid rain is of concern.

Like coal, most oil contains sulfur, including the desulfured residual oil commonly used for heating apartments, offices, commercial buildings and factories.

Most residual oil contains minute amounts of metals like vanadium that catalyze the conversion of SO_2 to sulfuric acid, some conversion taking place even before the gases leave the stack.

An EPA scientist studying emissions from four large oil-burning units in New York City found the boilers did indeed emit large amounts of both SO₂ and sulfuric acid. As suspected, vanadium was found in the oil, in the emissions from the boilers, and encrusted in the linings of the boilers where combustion takes place. EPA's investigators concluded that more than half the winter-time sulfate emissions in the New York City area are attributable to local oil-burning boilers, most of which typically have less well-controlled combustion than do the boilers of electric utility plants.

Findings such as these are preliminary. They need to be expanded and confirmed by other investigators. They do not preclude the possibility

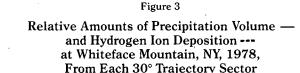
that emissions from coal-burning power plants in the Midwest contribute to the acidity of precipitation in the East, but they do cause doubts that the midwestern power plants are the principal factors accounting for acid rain in the Adirondacks and in Canada.

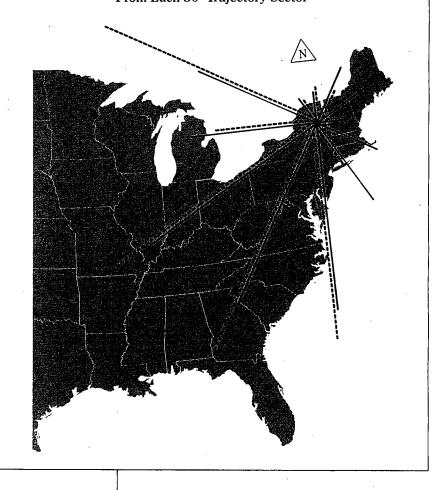
The relative importance of local or nearby emissions is further illustrated by the findings of a North Carolina professor who reported a positive correlation between the air pollution index in Charlotte, NC, and the pH of rain that fell 15 miles away.

Another recent finding is that of scientists at New York State's Atmospheric Sciences Research Center, who made detailed analyses of precipitation at Whiteface Mountain, high in the heart of the Adirondacks. Precipitation volume and the amounts of rain components for the year 1978 were compared against the meteorological data that traced weather backwards for two days prior to its arrival at the observation station. The researchers found that hydrogen ion deposition roughly paralleled the amount of precipitation, regardless of the direction from which the weather had arrived. When the analysis is confined to the sector that includes Illinois, Indiana and Ohio, the arriving weather was found to have brought 36 percent of the precipitation and 40 percent of the hydrogen ions. Moreover, 26 percent of the precipitation and 31 percent of the acidity arrived from the sector covered by the Upper Great Lakes and Canada (Figure 3).

This pattern was not unique for Whiteface Mountain. A similiar relationship was found at Urbana, Illinois, for the same year. It is evident, at least for these two locations, that inch for inch of precipitation, acid deposition remains remarkably consistent regardless of the direction from which the weather arrives.

As the perspective broadens, the case is strengthened against the idea that long-range transport of midwestern emissions influences eastern acidity.





THE EFFECTS OF ACIDITY

espite publicized fears, warnings and predictions of dire effects from acid rains, there is little evidence that variations in acidity have had adverse impacts on the environment.

Agricultural resources have been said to be vulnerable, but the only verified reports of impacts on plants are where there was prolonged exposure to acidity at artificially high levels in laboratory conditions. The Environmental Protection Agency treated 28 varieties of plants under greenhouse conditions with artificial rain adjusted to pH 4.0, 3.5 and 3.0, with mixed results. More than half the varieties showed some leaf damage, but this did not always coincide with effects on plant yield. In fact, while 40 percent of the varieties showed decreased yields and 20 percent showed no effect, 40 percent showed increased yields under increased acidity.

Grain crops proved to be tough and suffered neither leaf damage nor reduced yields.

At pH 3.0, corn yields increased by 11 percent, tomatoes by 30 percent and strawberries by more than 70 percent. Peppers showed increased yields at pH 3.5 but reduced yields at pH 3.0. Carrots, beets and radishes were adversely affected by lowered pH and so were snails, beetles, and other insect pests.

Beneficial effects from exposure to acid rain are explained in part by the fertilizing value of the extra nitrogen and sulfur in the rain. In addition, the more acidic the rain, the greater the solubility and therefore the availability, of some of the soil's nutrients.

Fears that acid rain can damage forestry resources have been voiced but not substantiated. either. Experimental exposure of trees, seeds and seedlings to artificial acid rain has produced varying effects, some of which are beneficial and some adverse. A study for the paper industry found no confirmed evidence that the acidity of rainfall in the natural environment had a detectable impact on plants or trees.

This absence of verifiable damage in the plant world is not surprising. Variation in the environ-

ment is part of nature's plan; different varieties thrive in differing environments. Azaleas. rhododendrons and evergreens do better with high-acid fertilizers while grass, flowers and vegetables call for low-acid nutrients. Lawns look better when they have been properly limed to raise the pH, but many yards have a satisfactory look even when people fail to check the soil pH or to correct for the acidity that has built up over time. Moreover, plants are remarkably resilient to

natural variations in their environment. Everything is greener following a good thunderstorm that brings not only increased acidity but increased nitrogen to the soil and plants. Researchers have had to resort to artificially strong and prolonged exposure to produce adverse changes in plant appearance or productivity.

The impact of acidity on aquatic life is more complicated to assess. Exposing fish to enhanced acidity does affect their life cycle. With increasing acidity, the fertility of eggs is reduced, followed by impaired ability of eggs to hatch and then for the fish to mature. It takes a major lowering of pH to affect adult fish. Canadian researchers found that smallmouth bass stop reproducing at pH 5.5-6.0. lake trout at pH 5.2-5.5, rock bass and brown bullheads at pH 4.7-5.5 and lake herring, yellow perch and lake chub at pH 4.5-4.7.

Fishkills associated with surges in lake acidity have been reported from Europe where they were noted following sudden spring thaws. Accumulated acidity may have come from the snow itself, but some of it has been traced to the bacterial activity in decaying ground cover and soils even while they were blanketed with snow. A sudden flush of acidity may overwhelm the natural buffering capabilities of a body of water and significantly lower its pH for a period of time.

Most lakes are not seriously affected by the acidity of rainfall. This is partly due to the organic and mineral materials naturally present in the water or on the lake bottom that buffer the lake's chemistry and keep it fairly constant. More important are the effects of the leaf canopy, vegetation

There is little evidence that variations in acidity have had adverse impacts on the environment

and soils that surround the lake and act as an absorbent and neutralizer for precipitation acidity. Since the watershed surrounding a lake or pond is often much larger in area than the lake or pond itself, these environmental modifiers often have a major role in modifying the water before it reaches the lake. Where the lake itself and its surrounding terrain are low in buffering capacity, the lake can then be subject to major impact from the rainfall it receives.

cipitation acidity on lake chemistry and biology is the Integrated Lake Watershed Acidification Study being conducted by the Electric Power Research Institute. Panther, Sagamore and Woods Lakes in the heart of the Adirondacks are close enough to-5.5 for Woods Lake. These differences in pH are explained in part by the differences in the geological make-up of the lakebeds and the surrounding soils.

There is no question that the acidity of precipitation can affect the lakes into which it falls or flows, but the newer understanding of the dynamics of lake chemistry weakens the idea that it is primarily the acidity of precipitation that determines the survival of fish. In fact, the varied and complex interacting influences make it impossible to pinpoint any single factor as being the major determinant of lake acidification or of fish loss.

Damage to architectural stone surfaces has been connected with atmospheric acidity, but the major cause appears to be the impact from local sources of air pollutants such as heavy vehicular traffic, oil refining and industrial activity. Moreover, impacts from air pollution in general and impacts from acidic precipitation cannot be distinguished.

A flurry of news articles alleging an impact of acid rain on automobile finishes appeared in late 1980, but these stories were unfounded except as they related to acid smut fallout on vehicles parked

The most extensive study of the impact of pregether so that the rain falling in each of the lakes is similar if not identical in chemical make-up. Yet the three lakes have quite different pH values—pH 7.0 for Panther, pH 5.5 to 7.0 for Sagamore and 4.4 to

near the offending chemical plants. Acid smut is often a matter of the deposition of acidic particles quite unrelated to acid rain.

Another alleged hazard is the effect of acid waters on metal pipes. Both copper and lead pipes are relatively untouched by moderately acid solutions, and none of the feared health impacts have been documented. In most cases, any precipitation would be partly or completely neutralized as it seeps from the surface through the soil to underground pools or wells.

All in all, the effects of acidity on the environment have not been found to be as severe as some have suggested and the feared impacts have not been demonstrated outside the laboratory. When lake acidity is considered carefully, it is evident that lake chemistry is influenced strongly by many factors other than precipitation. It remains prudent to continue to study the impacts of acidity on the environment, but the evidence does not support panicky, sensationalistic fears.

Beneficial ef-

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are explained in

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NEW YORK'S ADIRONDACKS

A SPECIAL CONCERN

Adirondack Park



ix million acres of northern New York State are set aside as the Adirondack Park, the largest in America. It is a wilderness with high mountains and sparkling lakes and streams. It is relatively undeveloped but has forestry resources that bring important revenue to the state. It is sparsely settled by permanent residents and is a recreation site for thousands of visitors who enjoy a variety of activities there, not the least of which is sport fishing.

Fishing has been enjoyed in the Adirondacks for generations by people from all walks of life. Some of the wealthy with summer homes in the region fished for trout there more than a century ago, and when there were fewer fish than they and their guests desired, they had the lakes restocked. Later, like most other states, New York adopted conservation programs and replenished the fish.

There are more than 2,800 lakes and ponds in the Adirondack Park, ranging in size from less than one acre to Lake George with 28,000 acres. Concern about the fish populations of the Adirondacks goes back more than half a century, when a number of studies were conducted and some lakes were selected for restocking programs to assure continuing sport fishing.

As acid rain emerged as an environmental issue, it became convenient to point to it as the cause of poorer fishing in Adirondack lakes. This prompted a Cornell University scientist to survey 124 high elevation ponds, more than half of which had surface pH values below pH 5.0.

With that, the war against acid rain in New York began. New York government officials became active participants in the attempt to reduce the impacts of acid rain on state resources, and they have marshalled the media to report the damage as well as measures intended to fight acidity.

Despite major research efforts by a large group of concerned individuals and agencies, the evidence of widespread damage from acid rain remains less than convincing.

The 1980 report of two researchers of New York's Environmental Conservation Department

Restocking efforts were kept up for many years, but in every case the annual additions of fish were eventually reduced and finally stopped especially is revealing. Despite their conclusion that precipitation acidity is threatening the aquatic life of the Adirondacks, they had no data to show that acidity increased in any of the lakes since they had disregarded pre-1975 data because of its questionable reliability.

Their efforts also provide narrative histories of 12 Adirondack lakes "whose fish populations have either been entirely eliminated or dramatically reduced as a result of acidification."

Those waters were all said to have had fish when checked in the 1930s or earlier, but at that time all 12 lakes in fact were being restocked annually from fish hatcheries to assure the maintenance of good fishing for sportsmen. For example, 500 fish annually went to 38-acre Horn Pond and 22,000 fish annually for 499-acre South Lake. In many cases, the varieties added were changed in the hope of improving the success rate for survival and reproduction in these lakes which even then were having trouble supporting fish life. Restocking efforts were kept up for many years, but in every case the annual additions of fish were eventually reduced and finally stopped.

One fact emerges from these histories: these lakes and ponds were *not* hospitable environments for sport fish 50 or more years ago.

The narratives mention that pH was generally above 6, despite the rejection of early data in another part of the report. In light of what is known now about discrepancies between pH determined colorimetrically and by other methods, the pH values in this report were not only of questionable reliability but were quite likely to have been artificially higher than the true values.

One lake has an especially interesting history. Cranberry Lake had been good for trout fishing until the 1950's when there was an explosive increase in perch at the expense of the trout. This has been attributed to changes in the lake's chemistry as a result of beavers damming tributaries, forest fires and logging practices. The restocking program there was terminated in the 1950s. Recently, for reasons not established, the

believe.

perch population has been dwindling and brook trout have begun to return to Cranberry Lake. The role of acid precipitation in this natural history story is not clear, but it is hardly likely to have been as significant as some would like people to

Another interesting element in the Adirondack acidity story is the presence of plant life around some of the more acidic lakes that suggests those lakes have been this way for a long time. A leading limnologist noted that much of the plant life was indeed consistent with acidic waters, and observed that the blueberry bushes and other shrubs indicate the acidity was not of recent origin.

If the notion is valid that power plant emissions from the Ohio River Basin influence the acidity of precipitation in upstate New York, it would be expected that acidity patterns would be very similar for places along the path of the air masses that carry the emission products eastward.

Research does not support this notion.

Among the sites where the U.S. Geological Survey has sampled and analyzed precipitation since 1965 are three that lie pretty much on an east-west line along the center of New York State: Mays Point, near Syracuse; Hinckley, about 100 miles to the east, near the southwest corner of the Adirondack Park; and Albany, about 80 miles south east of Hinckley.

The acidity patterns for these three sites are far from similar. At Mays Point, the pH was generally lower from 1965 through 1967, while at Hinckley, there were several periods of elevated pH values. From 1968 through 1971, the patterns were reversed: low pH at Hinckley but periods of less acidity at Mays Point. The readings at Albany are not related to those at either of the stations to the west—"upwind" if the Ohio-to-Adirondacks air mass movement pattern really held (Figure 4).

There are no explanations for these differences in patterns of precipitated acidity. But the evidence from the Geological Survey shows they certainly were not similar, making it hard to believe that emissions from power plants 400 to 800 miles to

ACID RAIN

the west in Illinois, Indiana and Ohio directly influence the acidity of rainfall in upstate New York.

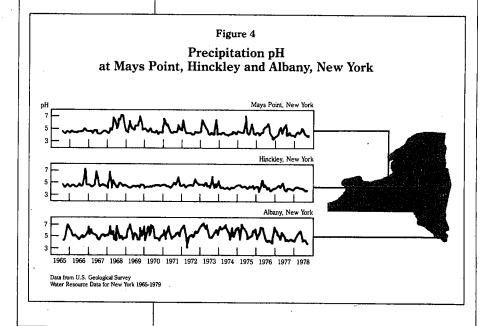
Although New York's Adirondack region is one of the focal points of interest and major concern about the presence and effect of acid rain, the facts do not support the widely held impression that emissions from the Midwest are causing problems in The Empire State.

Corrective measures are difficult to design when the problem cannot be clearly defined with the evidence at hand:

☐ Much of the rain in New York is indeed acidic, but there are no data to support the claims that the rain is becoming *increasingly* acidic.

☐ The most substantial data show that acidity fluctuates continually and the differences in patterns at places within 100 miles of each other suggest that they are *not* under the dominant influence of emissions from places 400 to 800 miles away.

☐ At least for 1978, less than one-third of the precipitation and about four-tenths the acidity could



The available evidence certainly is not consistent with the charge that rain is becoming increasingly acidic

be meterologically traced to the sector that includes Illinois, Indiana and Ohio. Regardless of the direction from which the weather arrived, acidic deposition was closely related to precipitation volume; inch-for-inch of rain, the acid deposition remains substantially constant.

☐ Many lakes have pH values less than 5.0, but the evidence does not support the allegation that the lakes have become more acidic in recent years.

□ Some lakes may well have poor fishing now, but there is reason to believe that many of them were less than hospitable to fish as much as 50 years ago and provided good fishing only because they were regularly restocked with the trout that fishermen prefer.

Looking at all the information now available, precipitation in the Adirondacks seems far less hazardous to the environment there than some of the sensationalistic statements suggest. Indeed, the reality of the evidence makes it difficult to believe that conditions in the Adirondacks are much different now from those of over the last twenty years and perhaps the last half century.

12 CORRECTIVE STRATEGIES

eep concerns about precipitation acidity have led to a variety of proposals aimed at reducing acidity or overcoming its effects. One of the most controversial suggestions is to require older coal-burning power plants in and around the Ohio River/Midwest region to be fitted with stack gas "scrubbers" to reduce further their emissions of sulfur and nitrogen oxides.*

What benefits could reasonably be expected from retrofitting older plants with scrubbers as has been suggested? So far, there is little evidence that real benefits would be realized. Even if SO₂ and NO_x emissions were reduced in the Ohio River/Midwest region power plants, there is no evidence that this would have significant effect on the acidity of precipitation in the northeastern U.S. or in Canada. There is also no convincing evidence that detectable changes in the acidity of lakes or streams or the aquatic life they support would occur.

Why not try scrubbers anyway, to see whether they could help? A stack gas scrubber for a coalburning power plant entails an investment of around \$100 million to \$250 million for equipment alone. Moreover, scrubbers take energy to operate, so that 3 percent to 6 percent of a plant's power output has to be turned back directly into the operation of this equipment. Other costs, including the purchase of chemicals and the disposal of the sludge collected from scrubbing, add further to the plant's operating costs. Disposing of that sludge actually imposes an additional problem for those concerned with a clean environment.

Scrubbers take energy to operate, so that 3 percent to 6 percent of a plant's power output has to be turned back directly into the operation of this equipment

Different types of scrubbers are in use, but all operate on the same basic principle—scrubbing the combustion gases with a chemical solution. During the scrubbing process, the sulfur dioxide gas is trapped when it reacts with chemicals in the solution to form a new substance. The volume of this new substance, commonly called "sludge" can be considerable.

^{*}The Clean Air Act Amendments of 1977 forced all coal-burning power plants commencing construction after 1979 to be equipped with stack gas scrubbers. Plants built between 1971 and 1979 were exempt from the scrubber requirement but subject to maximum emission limitations. All power plants, regardless of age, are subject to emission limitations under State Implementation Plans.

Some proponents have argued that on the basis of the national average cost of electricity, the incremental costs for scrubbers would be quite small and affordable. In fact, however, each utility company's rates are set separately by a regulatory commission that considers costs on a case-by-case basis. A company with three plants, each of which might be required to retrofit with scrubbers, would have a much greater rate increase than a company with only one of perhaps ten plants needing the equipment proposed.

What other steps could be taken if cutbacks in SO₂ are either non-effective or prohibitive in cost?

The most promising strategy for helping lakes with low pH problems is to use lime or limestone to reduce the acidity and raise the pH. Liming has been tried in New York since the late 1950s, and although not always 100 percent successful, liming efforts have been increasingly promising. Many lakes that were completely barren of fish before liming have produced excellent fishing after treatment.

In Sweden, too, liming has had positive results. Salmon, trout and other species of fish have returned in numbers following treatment of acidified waters.

Apparently liming does more than simply raise the pH. Calcium, the principal constituent of lime, has a specific and beneficial effect on fish. Research has shown that the calcium content of lakes is probably more important than the pH in determining the ability of fish to survive and multiply.

Liming is a bargain when compared to the increased cost of electricity if retrofitting with scrubbers were to be imposed. According to one estimate, it would cost about \$4 million a year to raise the pH of 468 of the Adirondacks' most acidic lakes to pH 6 or higher. Compare this to estimated costs for the addition of scrubbers to 50 of the largest older coal-burning power plants east of the Mississippi: the Environmental Law Institute estimates \$7 billion to \$14 billion for capital costs and a \$1 billion to \$2 billion annual operating cost for this proposal; the Department of Energy's Morgan-

As of now, there simply are not enough facts to guide either government or industry in designing corrective steps that will bring predictable results

town. Energy Technology Center has developed estimates of \$11 billion for capital costs and \$3.6 billion for annual operating costs for this same proposal.

What is more, the benefits of liming can be realized within a year of starting treatment, while retrofitting power plants with scrubbers would take at least three to five years even to build. Since the legal basis for this requirement depends on amending the Clean Air Act, the regulatory processes involved would add many months or even years before plans were approved and construction could be started. Add to that timeframe the possibilities of unforeseen delays, and it becomes evident that this would be a slow approach to highly uncertain benefits that can alternatively be achieved within one year wherever liming is adopted.

Other strategies are under study as well. Biologists are trying to identify and breed varieties of trout and other species that are more tolerant of acidity or of the effects of acidity in combination with metal such as aluminum, long under suspicion as a danger to fish.

The electric power industry is continuing to seek ways to further reduce the emissions of sulfur and nitrogen oxides by means other than scrubbers. Better control of combustion seems to be beneficial in lessening NO_X emissions. And more economical means of removing sulfur from coal could lead to lowered SO_2 emissions.

As with so many other efforts to solve our social concerns, it is probable that controlling the acidity phenomenon will take a variety of measures working together. As of now, there simply are not enough facts to guide either government or industry in designing corrective steps that will bring predictable results.

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36

In this country, the electric power industry is committed to an extensive effort cid rain is still a puzzle. More than a dozen countries and international agencies are searching for causes and cures for acid rain, with the major efforts taking place in the United States, Canada, Great Britain, Norway, and Sweden.

In this country, the electric power industry is committed to an extensive effort. The Electric Power Research Institute, research arm of the entire power industry, has sponsored and coordinated research on acid rain for more than 5 years. It has spent more than \$15 million so far and more than \$17 million is targeted for future research. The coal industry and the petroleum industry are also very involved in acid rain research.

In the federal government, more than 10 agencies conduct a wide variety of programs. Most heavily involved are the Environmental Protection Agency, Department of Agriculture, Department of Energy and National Oceanographic and Atmospheric Administration. Other groups include the Fish and Wildlife Service, Forest Service, U.S. Geological Survey, Tennessee Valley Authority and the Council on Environmental Quality.

Government research totaled more than \$30 million in FY 1981, and Title VII of the Energy Security Act of 1980 calls for expenditure of an additional \$10 million in research annually through 1990.

This massive exploration is expected to answer such important questions as where atmospheric acidity comes from, how it is transported, how it affects the ecology and how those impacts can be lessened. Major research projects include:

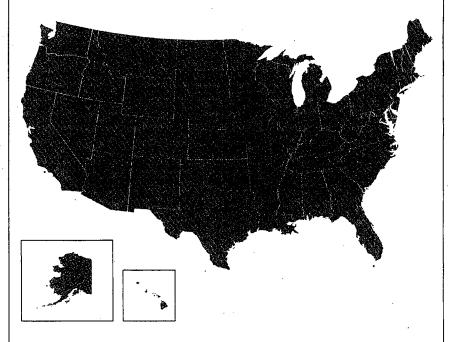
- ☐ Networks of rain sampling stations to collect and analyze precipitation and give a more complete picture of the chemistry of precipitation over extended periods of time. (Figure 5)
- ☐ Studies of air mass movements to explain how emissions from one area may be related to depositions in another place.
- $\hfill \Box$ Studies of the effects of rain on agricultural and forest resource productivity.

ACID RAIN

- ☐ Studies to learn how precipitation affects the chemistry of lakes and how this impacts aquatic life.
- ☐ Searches for new ways to reduce even further emissions of sulfur and nitrogen oxides from coalburning power plants by means other than retrofitting with expensive scrubbers.

The research effort is massive and expensive. Despite the professional optimism of scientists and administrators, no one expects the answers soon. Many now believe it will take another five years of collecting and analyzing data before there is

Figure 5
U.S. Precipitation Chemistry Networks



Over 200 monitoring stations collect precipitation for a variety of studies to provide weekly data for determining long-term trends and for intensive analysis of specific events and storms. Station at Hubbard Brook, NH, has operated continuously since 1963. The majority have operated since 1979; 4 networks are due to start up in 1981.

tive new laws and regulations.

major item in those negotiations.

St. Lawrence River.

enough information and enough understanding of acid rain to permit the writing of intelligent, effec-

International relations are also affected by the

acid rain controversy. The U.S. and Canadian gov-

ernments have embarked on a joint effort to stave

off disputes over the significance of emissions from midwestern power plants and the rain that falls on

the Canadian provinces along the Great Lakes and

The two nations are working toward a bilateral

agreement designed to "develop measures to con-

trol transboundary pollution", with acid rain as a

ble for environmental protection acknowledge that more facts are needed before corrective strategies can be prescribed.

ACID RAIN

It is too early to predict just how the matter will be resolved, but the facts now at hand contribute to a more optimistic picture than some of the sensationalistic reports would suggest.

A more meaningful perspective can be summarized this way:

□ pH 5.6 is wholly unrealistic as the reference point below which rain is considered unnaturally acidic. In many places around the world, including locations remote from industrial activity, the pH of rain is often more acidic than pH 5.6, frequently lower than pH 5.0.

☐ Far more than carbon dioxide contributes to the natural acidity of rain, and far more than sulfates and nitrates determine the acidity of rain wherever measured.

☐ Acid-neutralizing compounds of calcium, magnesium and ammonia significantly influence the acidity of rain, and these are important in explaining the differences in precipitation acidity.

☐ Claims that the rain is becoming increasingly acidic in the Northeast are not substantiated, nor are the claims that both the rain and the lakes of the Adirondacks are becoming increasingly acidic.

☐ Complaints about reduced fish populations in the Adirondack lakes are not accurately documented. There is evidence some of the lakes in question were inhospitable to fish in the 1930's and earlier.

☐ There is no evidence that the acidity of rain or of Adirondack lakes would be substantially altered if coal-burning power plants in the Ohio River Basin were required to install scrubbers.

IN SUMMARY

Acid rain is an issue that will not be resolved quickly

It is too early to predict just how the matter will be resolved, but the facts now at hand contribute to a more optimistic picture than some of the sensationalistic reports would suggest

☐ Claims that acid rain is damaging agricultural or forestry productivity are unsubstantiated, and there is no basis for translating controlled experiments with artificial environments to the natural systems.

It is far too early for responsible people to suggest that the feared consequences of precipitation acidity are unreal and will never be proved, but it is also too early to resort to the proposed corrective strategies without evidence of their probable effectiveness.

Government, scientists and industry are working toward an understanding of the phenomenon that should resolve the issue. Meantime, while the phenomenon of acidic precipitation continues around the world, the spectres conjured up by the use of the term "acid rain" seem to fade with each new addition to our base of knowledge.

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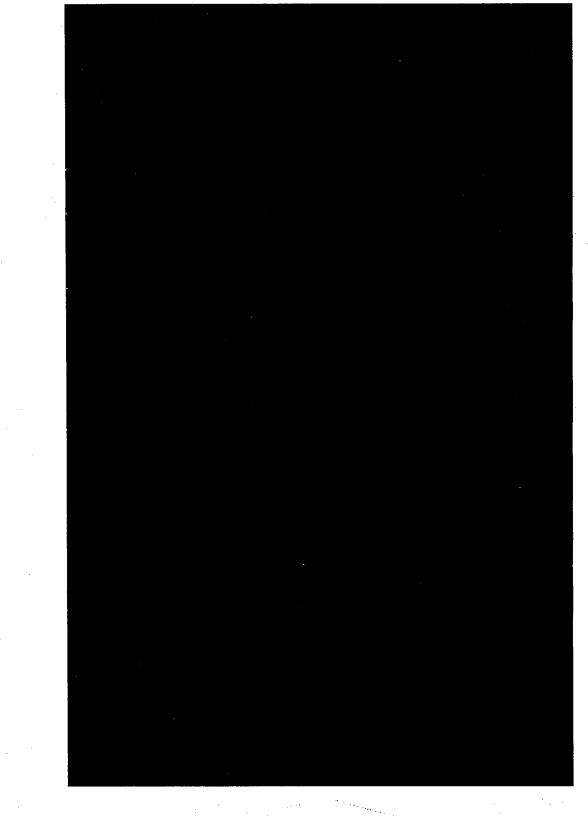
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